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pH Effect on the Arsenic Separation in Waste Water of Coal Based Power Plant

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To the Graduate Council:

I am submitting herewith a thesis written by Ye Hao entitled "pH Effect on the Arsenic Separation in Waste Water of Coal Based Power Plant." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Robert M. Counce, Major Professor

We have read this thesis and recommend its acceptance:

Paul R. Bienkowski, Jack S. Watson

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Simulation of pH Effect on the Arsenic Separation in Waste Water of Coal Based Power Plant

A Thesis Presented for
the Master of Science
Degree
The University of Tennessee, Knoxville

Ye Hao
May 2010

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Abstract

Arsenic (As) poses a significant water quality problem and it is a big challenge for all coal-based power plant industries worldwide. Currently most of the researches on the leaching behavior of arsenic from fly ash are based on the titration experiments. In this study a simulation method is used to study on the pH effect on the arsenic separation of coal-based power plants. Both single point and composition survey simulation of the OLI stream analyzer are used in the study. The simulation results of single point calculation indicates that for the fly ash which has high lime weight percent and equilibrium fly ash solution pH is over 11 and between 7 and 9, that is, Type C fly ash, the simulation results for equilibrium pH in fly ash solutions have great accuracy compared to actual experiment results. Based on the results obtained from single point simulation, both acid and base titrations of composition survey are simulated and the output results suggest that for the same type of fly ash, the simulation results proves the general trend of arsenic solubility in fly ash solutions. The solubility of arsenic decreases with the increase of pH value. It is also noted that at the equilibrium pH fly ash solutions, the maximum solid/liquid ratio of arsenic concentration is observed for type C fly ash. For other fly ashes which have low lime weight percent, the simulation results have discrepancy compared to actual experiment results. This work is important in offering an alternative way of analyze the reasonable output species and relative concentrations for type C fly ash in the waste water storage pond under specific pH conditions, which can be of great importance for the power plants to monitor and minimize the environment pollution in order to meet the future federal regulations.

Keywords: Arsenic; Leaching; Fly Ash; pH; OLI stream analyzer; Power plant

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction and General Information

1.1 Research Proposal

In this thesis capability is developed to predict the aqueous phase arsenic discharge from a coal-fired electrical power plant. Arsenic is a typical contaminant in coals and in such an electrical power plant most of the arsenic discharge will be associated with the combustion ash, fly ash and other residues from flue-gas treatment and water used to transport these materials. An example of such a plant is the Tennessee Valley Authority (TVA) Kingston Power Plant, which is one of the largest coal-burning power plants in US. One major problem of this kind of plant is the control of arsenic and other emissions. In this thesis the focus is on control of arsenic emission. Since utilities are required to meet current and anticipated future federal laws and regulations on water effluent discharge, this thesis is intended to aid in the prediction of potential arsenic emissions from such facilities.

1.2 Research Goal

The research goal is to develop capability to predict the arsenic concentration in the aqueous effluent of coal fired electrical power plant. The capability is demonstrated using different types of fly ashes solutions and various modes of arsenic control. The study uses the OLI SYSTEMS Stream Analyzer to predict the expected pH in the aqueous streams of interest and to simulate the possible leaching characteristic of arsenic in the waste water storage pond of power plant. The computing platform for the distribution of arsenic is processed in EXCEL. Limited data of arsenic leaching behavior from laboratory experiments will be compared to literature derived models predicting this quantity. The model is examined from a number of perspectives to assure its credibility.

Chapter 2

Literature Review

2.1 Process Description

The coal-based power plants are similar in design and operation so we take the Tennessee Valley Authority (TVA) Kingston Power Plant as an example. Arsenic in such facilities is associated with the combustion ash, fly ash and other residues from flue-gas treatment and water used to transport these materials. The ash, residues and transporting water are routed to a solid-separator, called an ash pond. In this separator the solids are separated from the aqueous phase, with the solids routed for disposal and the aqueous phase discharged or recycled. Such a system is shown in Figure 2-1 [1].

In a typical coal-based power plant, coal is pulverized into a fine powder and injected into the boiler where it is combusted. Relevant coal properties and composition are shown in Table 2-1 [1] .The combustion of coal illustrated as Step 1 in Figure 2-1, heats highly treated demineralized water in a boiler, changing the water into gaseous steam. The steam, at an elevated temperature and pressure, is throttled into a turbine, where the forces of the expanding steam spin the turbine blades. The turbine spins a magnet inside copper coils in a generator to produce the flow of electrons – electricity [1].

After Step 1, the flue gas from coal combustion contains CO_2, NO_x and SO_x as well as other constituents. The flue gas is shown in Figure 2-1 to pass through the Selective Catalyst Reduction Unit (SCR) for NO_x control. Ammonia is injected into the flue gas stream and introduced into the SCR, where in the presence of vanadium-titanium catalyst NO_x is converted to N_2 and H_2O. The flue gas then passes through the Electrostatic Precipitator (ESP), where the particulate solids are ionized and separated from the flue gas stream. Almost all the NH_3 and majority of the oxidized Hg are separated in the ESP with fly ash. The ash collected at the boiler bottom during combustion is the bottom ash and the ash collected in the ESP is the fly- ash.

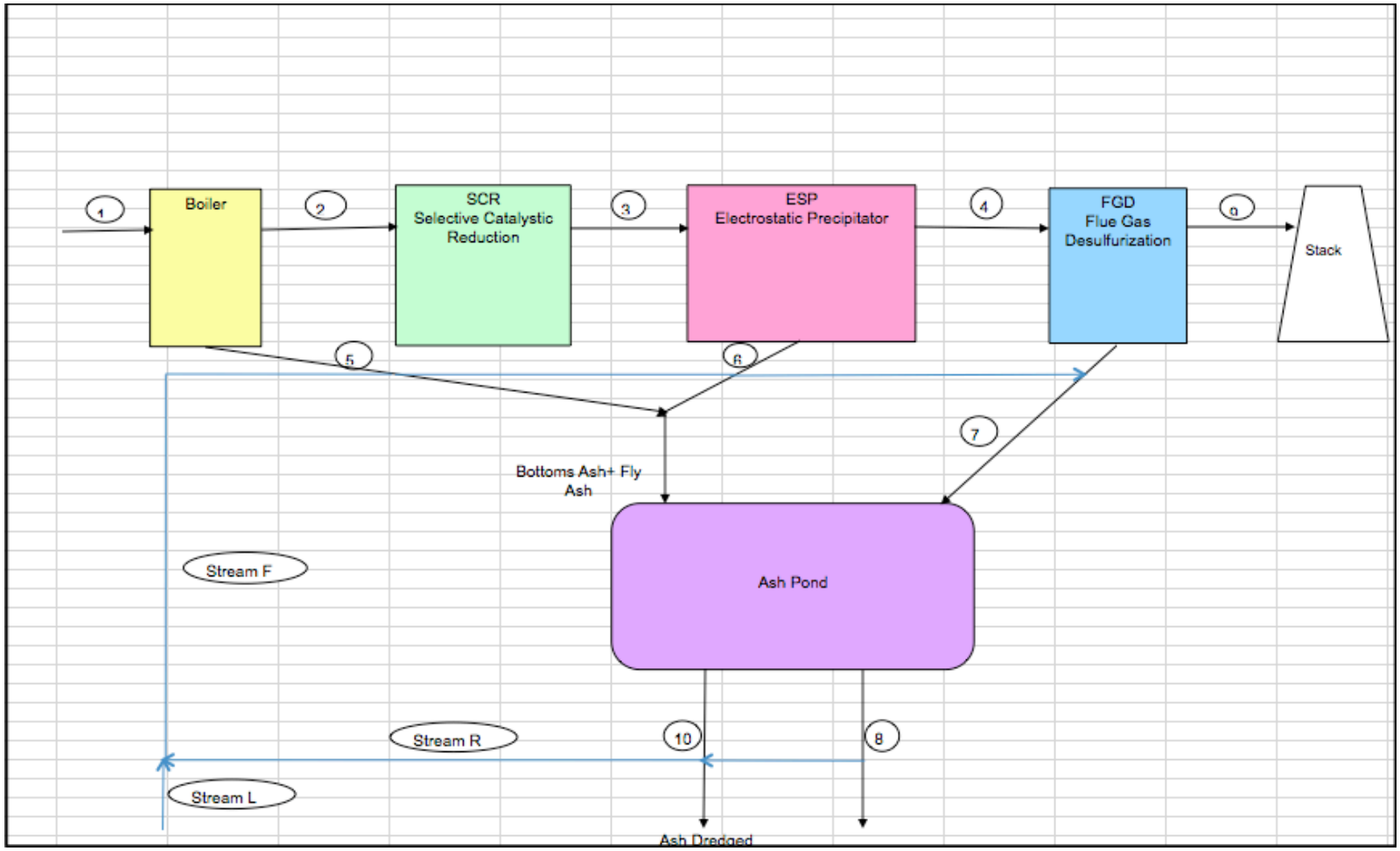


Figure 2-1 The chematic of the system for handling water, bottom ash and residues from flue-gas cleanup.

Table 2-1 Description of relevant coal blends.

	Blend1(PRB)	Blend2(PRB)	Blend3(Colorado)	Blend4(CAP)
Type	Sub-bituminous	Sub-bituminous	Bituminous	Bituminous
Coal (%)	68.31	67.98	79.19	78.22
Moisture (%)	26.04	26.05	11.2	7.04
Sulfur (%)	0.32	0.34	0.47	0.61
Ash (%)	5.33	5.63	9.14	14.13
Coal Composition (%)				
carbon, dry	69.1	68.8	73.3	68.5
hydrogen, dry	5.01	4.64	4.94	4.62
nitrogen, dry	0.94	1.04	1.62	1.05
oxygen, dry	17.3	17.4	9.33	16.4
chlorine, dry	0.006	0.011	0.04	0.007
phosphorus, dry	0.64	0.44	0.49	0.4
Arsenic	0.000007	0.00000683	0.00000574	0.00000751
Ash, dry	7.004	7.669	10.28	9.023

Source: Bratendu Bagchi, 2007, "Computer Modeling of Tennessee Valley Authority's Coal Based Power Plant at Kingston to Predict the Effluent to Emory River", Doctoral Dissertation in Chemical Engineering, University of Tennessee Knoxville.

The bottom ash and the fly ash are collected by the sluice water collection system and routed to the ash pond. Un-reacted NH_3 from the SCR system also reports to the ash pond. In the ash pond, the incoming stream is separated into solid and aqueous phases and discharged as two separate streams: one is a wet solid stream containing the ash and other solid residue; the other is the effluent aqueous stream that may be discharge or recycled.

2.2 Arsenic

2.2.1 Introduction of Arsenic

Among all the elements, arsenic ranks 20th in abundance in Earth's crust. It is widely distributed among various mineral species. Arsenic is mostly found as a component of sulfide ores especially with non-ferrous metals. Arsenic is widely distributed in the nature and the concentration varying from 0.1 ppb in Lake Superior to as high as 276,000 ppb in the Waiotapu Valley Rivers of New Zealand [2, 3].

Arsenic also exists in all kind of animals. Human body tissue generally has less than 0.3 ppm of Arsenic [4]. However, it is well known that arsenic has a very acute toxicity. The toxicity of an arsenic-containing compound depends on its valence state (zero-valent, trivalent, or pentavalent), its form (inorganic or organic), and the physical aspects governing its absorption and elimination. In general, inorganic arsenic is more toxic than organic arsenic, and trivalent arsenite is more toxic than pentavalent and zero-valent arsenic. The normal intake of arsenic by adults occurs primarily through ingestion and averages around 50 ug/d (range of 8-104 ug/d). Most (around 64 percent) of this amount is accounted for by organic arsenic from fish, seafood, and algae; the specific arsenic compounds obtained from these sources are arsenobentaine and arsenocholine, which are relatively nontoxic and are rapidly excreted in unchanged form in the urine. After absorption, inorganic arsenic accumulates in the liver, spleen, kidneys, lungs, and gastrointestinal tract. It is then rapidly cleared from these sites but leaves a residue in keratin-rich tissues such as skin, hair, and nails. Arsenite (+V) undergoes biomethylation

in the liver to the less toxic metabolites methylarsenic acid and dimethylarsenic acid; the biomethylation neutron can quickly become saturated, however, and the result is the deposition of increasing doses of inorganic arsenic in soft tissues. Arsenic, particularly in its trivalent form, inhibits critical sulfhydryl-containing enzymes. In the pentavalent form, the competitive substitution of arsenic for phosphate can lead to rapid hydrolysis of the high-energy bonds in compounds such as ATP [5].

2.2.2 Usage of Arsenic

Arsenic is used for various purposes. The greatest consumption is in agricultural chemicals. Lesser amounts go to wood preservative, glass, alloys and electronics. The commonly encountered oxidation states of arsenic are +III valent as in As_2O_3 and +V valent as in As_2O_5 [4]. Formally a +III valent oxidation is assigned to AsH_3. The trioxide is moderately soluble in water but dissolves easily in alkali to produce a solution of arsenite, AsO_2- [6]. Arsenic trioxide is used for the treatment of certain forms of leukemia and other forms of cancer [7]. Arsenic was also long used as an agent in hide tanning, and as a pigment for paints and dyes, thereby becoming one of the first recognized chemical occupational hazards [8]. Arsenic in the form of cacodylic acid (dimethyl arsenic acid), under the code name agent blue, was used as a herbicide in the Vietnam war prior to the controversial application of agent orange. These past uses, although some are still employed nowadays, have had the effect of introducing a large cumulative quantity of anthropogenic derived arsenic into the environment which is always a potential hazard to the environment.

2.2.3 Arsenic Cycling in the Environment

Arsenic in aqueous medium such as ground water exists primarily as arsenite (+III) or arsenate (+V). These are the dominant inorganic forms in ground water (see Figure 2-2) [9]. Arsenate (+V) generally is the dominant form in oxic waters while arsenite dominates in sulfuric and methanic waters.

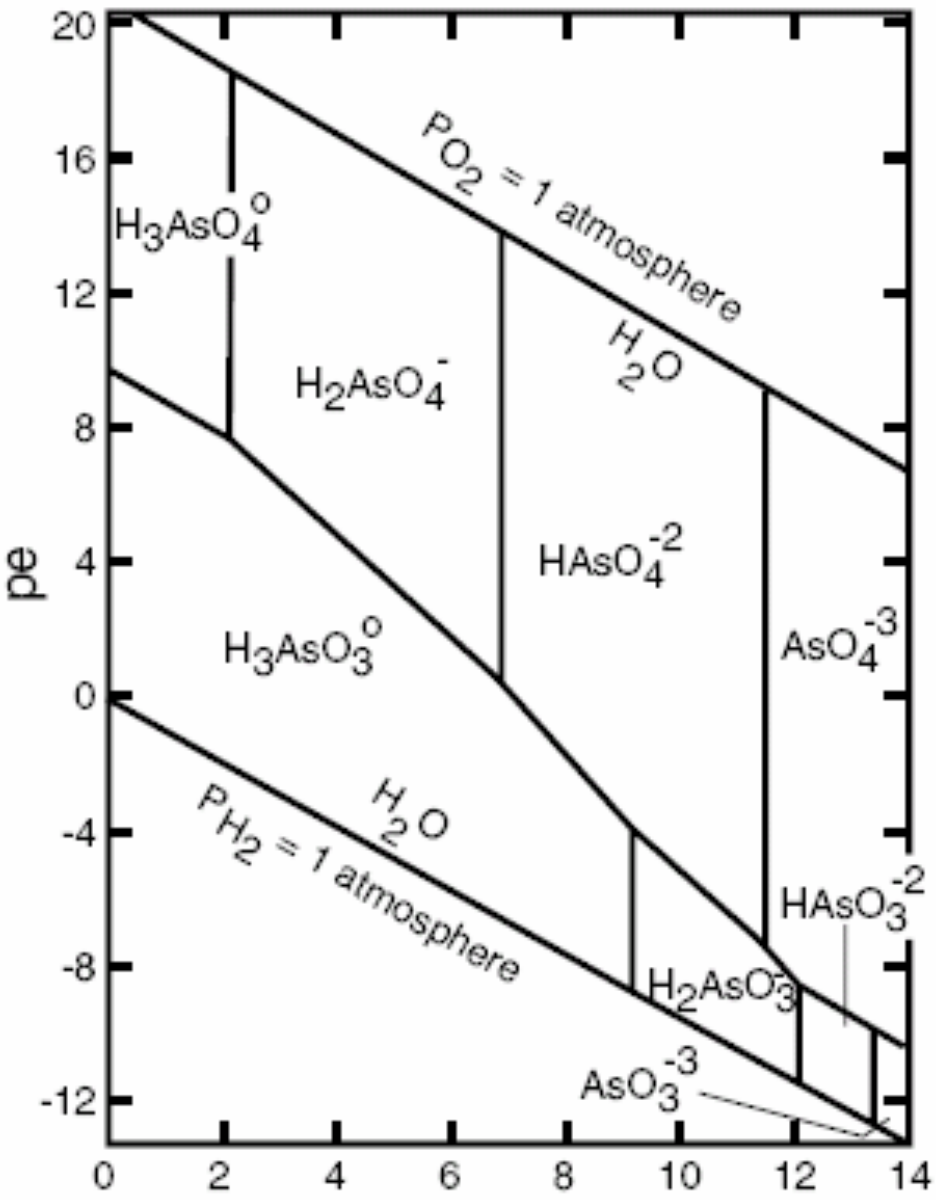


Figure 2-2 Aqueous arsenic dominance diagram at 25°C.

Source: Ball, J. W. and D. K. Nordstrom, 1991, "User's manual for WATEQ4F, with revised thermodynamic data base and text cases for calculating speciation of major, trace, and redox elements in natural waters". U.S. Geological Survey Open-file report, 91-183.

There are also other references related to the aqueous arsenic carbonate species in natural water [10, 11]. In highly reducing, sulfide-rich water, thio-arsenites (mono-, di-, and tri-) can form [12, 13].

The most common source of arsenic in groundwater is release from aquifer materials, although anthropogenic inputs have a significant source in some cases [9, 14, 15]. In the near surface, environmental arsenic cycles between ground water and a variety of aquifer materials. Chemical weathering of uplands commonly leads to the formation of iron oxide coatings on sediment. This weathering also releases arsenic that adsorbs or co-precipitates with the iron oxide.

After deposition, several processes can cause the release of the arsenic from this sediment into ground water [4]. An increase in pH can lead to desorption of arsenic from iron oxides. Two common causes of high pH ground water are silicate hydrolysis and calcite dissolution enhanced by cation exchange [9, 15]. Hydrolysis of common silicate minerals such as feldspars can produce progressively higher pH values along a ground-water flow path. Consequently, in a given system older ground water may have more arsenic because of the higher pH. Silicate hydrolysis of felsic volcanic rocks can produce fairly high pH in relatively young ground water, which is a contributing factor to the common association of high arsenic with this rock type [9, 16].

A second process that can cause a pH increase is exchange of sodium on sediments for calcium and magnesium in ground water, which enhances carbonate mineral dissolution [4]. High pH and arsenic concentrations associated with sediments that were in contact with continental brines formed by evaporation in a closed basin have been documented in northern Nevada. Deposition of iron oxide along with sedimentary organic matter is a common feature of basin-fill deposits and these two phases can react and release arsenic present in the oxide. This reaction is a commonly invoked cause of

high arsenic in ground water. The reaction increases the pH and releases iron, carbonate species and arsenic into ground water as represented by the following reaction [17]:

$$FeOOH + CH_2O + H_2O \rightarrow 4Fe^{2+} + HCO3^- + 7OH^- \quad \text{(2-1)}$$

The most common arsenic minerals in aquifer materials include arsenic-rich pyrite (FeS_2) and various arsenic sulfide phases that can form authigenically in sulfidic environments [18, 19]. Arsenic in trace amounts is commonly present in pyrite, but can reach concentrations as great as 8.5 percent [19]. The arsenic sulfide As_2S_3can form abiotically or biotically from non-thermal water and from geothermal water [4]. Oxidative dissolution of these sulfide minerals can cause the release and redistribution of arsenic in the aquifer as As (+III) and As (+V). Although pyrite oxidation is a complex chemical process that may involve 15 or more steps, the reaction is commonly written as [20]:

$$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow FeOH_3 + 4H^- + 2SO_2^- \quad \text{(2-2)}$$

$FeOH_3$, a product of reaction (2-2), can incorporate some of the released arsenic through adsorption or co-precipitation. Accordingly, quantitative release of arsenic into ground water should not be expected. Clay and other aluminosilicate minerals are known to be significant adsorbents of arsenic. With the possible exception of sediments of the Bengal Basin, these phases have not been identified as an important source of widespread high arsenic concentrations in ground water. [4] Only recently has a clear association of high As (+III) concentrations with weathered biotite been demonstrated through the use of spectroscopy and chemical extractions precipitation process [21]. Lin and Puls [22] investigated about the effects of aging on desorption of As (+III) and As (+V) from clay minerals (caused by adding phosphate for 10 hours) and concluded that the relative contributions of mass transfer and chemical hysteresis to the amount of slow desorption are not very clear.

2.2.4 Arsenic Compounds

The common compound forms of arsenic are halides, oxides, sulfides and hydride. Table 2-2 [23] describes the detailed categories of arsenic compounds. Table 2-3 and Table 2-4 [23, 24] show the physical and thermodynamic properties of some arsenic compounds.

2.3 Arsenic in Coal

2.3.1 Estimation of Coal Clarke Value of Arsenic

As it mentioned above, the widespread occurrence of the arsenic forces researchers to find its sources. Coal is one of these sources. In 2004, the coal Clarke values (World averages) of arsenic was recalculated using the successive averaging from minor (one coal bed) to large (totality of the coal basins) [25]. Modern estimations of arsenic Clarke values are based on approximately 185 random samples, derived from more than 43,000 analyses and details can be obtained in Figure 2-3 [26]. From this chart, the arsenic Clarke value for bituminous coals is 9.0±0.8 ppm. For lignite's (brown coals), it is 7.4±1.4 ppm. The corresponding new figures for ashes are 50±5 and 49±8 ppm, respectively.

Among the U.S. coal basins (provinces), the highest arsenic average is in the Appalachian basin (13.3 ppm) and Western Interior (12.2 ppm) provinces. In the other five provinces, arsenic averages vary from 1.8 ppm (Rocky Mountains) up to 7.3 ppm (Illinois). Over the smaller coal-bearing areas, the highest Arsenic content is in the southern Appalachians, 29.4 ppm. The overall average for all U.S. coals is 6 ppm [26].

2.3.2 "Coal Affinity" (coalphile coefficient) of Arsenic

"Coal affinity" (coalphile coefficient) is the ratio of Clarke value in coal ash/Clarke value in sedimentary rocks. For arsenic, this ratio is 50 ppm/11 ppm=about 4.5. Therefore, arsenic is a coalphile element. However, because of strong variation of the mean arsenic contents over the different coal basins, this value can vary sharply.

Table 2-2 Categories of arsenic compounds.

Halides	
Tri-halides	$As + 3F \rightarrow AsF_3$ $As + 3Cl \rightarrow AsCl_3$ $As + 3Br \rightarrow AsBr_3$ $As + 3I \rightarrow AsI_3$
Penta-halides	$As + 5F \rightarrow AsF_5$ $As + 5Cl \rightarrow AsCl_5$
Diarsenic Tetrahalides (They are known as lower halides)	$2As + 4Cl \rightarrow 2AsCl_4$ $AsCl_4 \rightarrow AsCl_4^- + As$
Oxides	
Trioxide	$4As + 3O_2 \rightarrow As_4O_6$ $As_4O_6 + 6H_2O \rightarrow 4H_3AsO_3$
Pentoxide	$As + 5HNO_3 \rightarrow H_3AsO_4 + H_2O + 5NO_2$
Sulfides	
Tri-sulfides	$As^{3+} + S^{2-} \rightarrow As_2S_3$
Penta-sulfides	$As^{5+} + S^{2-} \rightarrow As_2S_5$
Hydride	
Hydride	$H_3AsO_4 + 6H \rightarrow AsH_3 + 3H_2O$

Source: David R. Lide, 2006, “CRC Handbook of chemistry and Physics”, CRC Press.

Table 2-3 Physical properties of some arsenic compounds.

Compound	Formula	M.P (°C)	B.P (°C)	Density (g/L)
Arsenic	As	N/A	N/A	5.75
Arsine	AsH_3	-116	-62.3	3.18
Di-arsine	As_2H_6	N/A	N/A	N/A
Arsenic acid Hemihydrate	H_3AsO_4•0.5H2O	35.5	N/A	-2
Arsenious acid	H_3AsO_3	N/A	N/A	N/A
Arsenic diiodide	As_2I_4	137	N/A	N/A
Arsenic disulfide	As_2S_4	320	565	3.5
Arsenic bromide	$AsBr_3$	31.1	221	3.4
Arsenic chloride	$AsCl_3$	-16	130	2.15
Arsenic fluoride	AsF_3	-5.9	57.8	2.7
Arsenic iodide	AsI_3	140.9	424	4.73
Arsenic oxide	As_2O_3	274	466	3.86
Arsenic selenide	As_2Se_3	260	N/A	4.78
Arsenic sulfide	AsS_3	310	707	3.46
Arsenic chloride	$AsCl_5$	50	N/A	N/A
Arsenic fluoride	AsF_5	-79.8	-52.8	6.94
Arsenic sulfide	As_2S	Decomposes	N/A	N/A

Source: 1, David R. Lide, 2006, "CRC Handbook of chemistry and Physics", CRC Press. 2, Carl Yaws, 1999, "Chemical Properties Handbook: Physical, Thermodynamics, Environmental Transport, Safety & Health Related Properties for Organic & Inorganic Chemical", McGraw-Hill Press.

Table 2-4 Thermodynamic properties of some arsenic compounds

Compound	Formula	Crystal ΔH_f^0 ΔG_f^0 S^0 (KJ/ mol KJ/mol J/mol. K)	Liquid ΔH_f^0 ΔG_f^0 S^0 (KJ/ mol KJ/mol J/mol. K)	Gas ΔH_f^0 ΔG_f^0 S^0 (KJ/ mol KJ/mol J/mol. K)
Arsenic	As	35.1,N/A, N/A	N/A	302.5, 261.0, 174.2
Arsenic Bromide	$AsBr_3$	-197.5, N/A, N/A	N/A	-130.0, -159.0, 363.9
Diarsenic	As_2	N/A	N/A	222.2, 171.9, 239.4
Arsenic acid hemihydrate	H_3AsO_4-•0.5H2O	N/A	N/A	N/A
Arsenic acid	H_3AsO_4	-906.3, N/A, N/A	N/A	N/A
Arsenic diiodide	As_2I_4	N/A	N/A	N/A
Arsenic disulfide	As_2S_4	N/A	N/A	N/A
Arsenic bromide	$AsBr_3$	N/A	N/A	-130, -159,N/A
Arsenic chloride	$AsCl_3$	N/A	-305.0, -259.4, 216.3	-261.5, -248.9, 327.2
Arsenic fluoride	AsF_3	N/A	-821.3, -714.2, 181.2	-785.8, -770.8, 289.1
Arsenic iodide	AsI_3	-58.2, -59.4, 213.1	N/A	-58.2, -59.4, 388.3
Arsenic oxide	As_2O_5	-924.9, -782.3, 105.4	N/A	N/A
Arsenic selenide	As_2Se_3	N/A	N/A	-639.73, -569.02, N/A
Arsenic sulfide	As_2S_3	-169.0, -168.6, 163.6	N/A	N/A
Arsenic hydride	AsH_3	N/A	N/A	66, 68.9, N/A
Arsenic fluoride	AsF_5	N/A	N/A	-1069.43, -1172.36, N/A
Arsenic sulfide	As_2S_5	N/A	N/A	N/A

Source: 1, David R. Lide, 2006, “CRC Handbook of chemistry and Physics”, CRC Press.

2, Carl Yaws, 1999, “Chemical Properties Handbook: Physical, Thermodynamics, Environmental Transport, Safety & Health Related Properties for Organic & Inorganic Chemical”, McGraw-Hill Press.

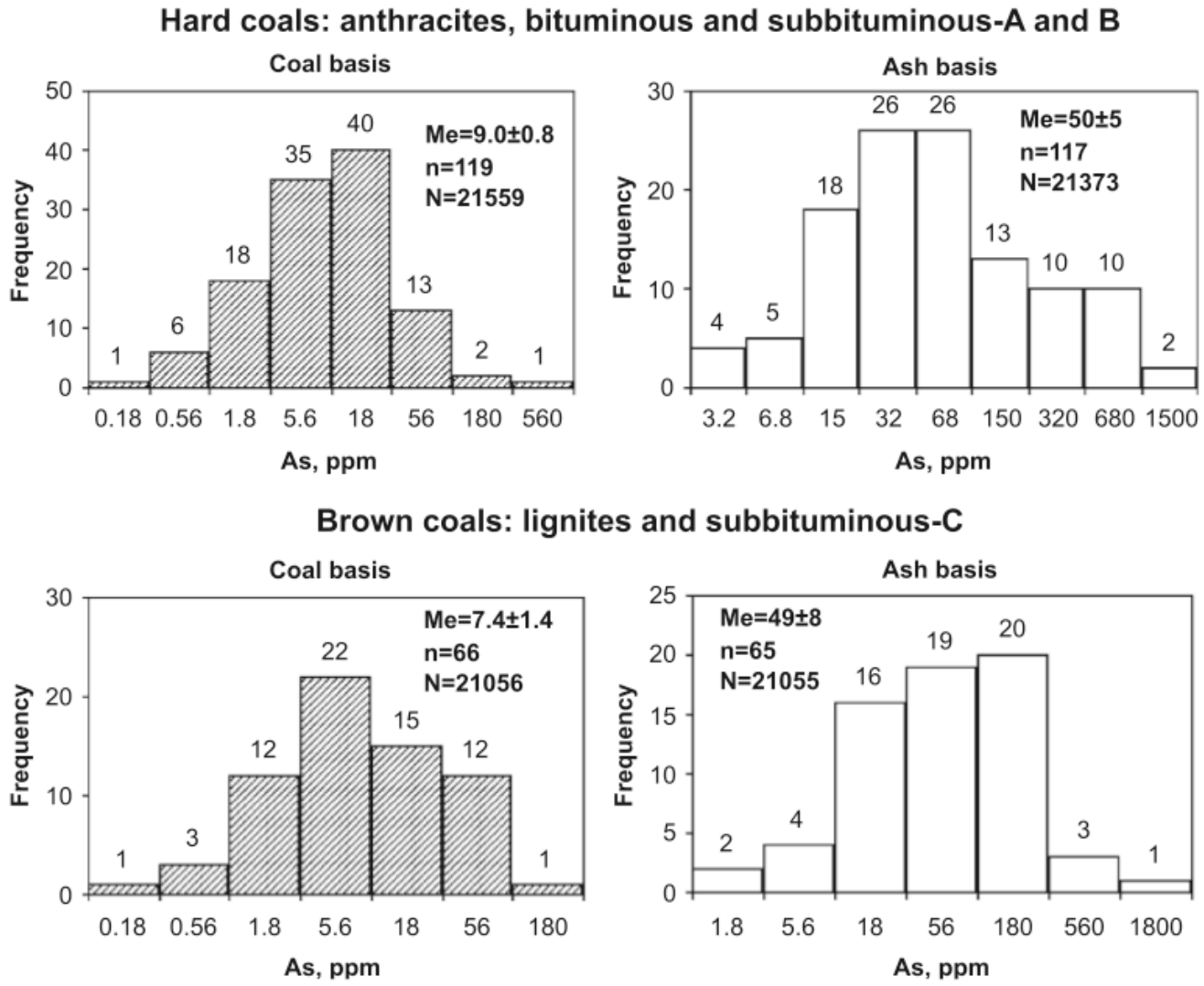


Figure 2-3 Frequency distribution of arsenic in world coals. N-number of analysis, n-number of random samples, Me- a median content.

Source: Ya.E. Yudovich, M.P. Ketris, 2004, "Arsenic in coal: a review", International Journal of Coal Geology 61, (2005), 141-196.

The coals notably enriched in arsenic above the Clarke level are rather widespread- they include the bituminous, lignite and sub-bituminous coals. In U.S. among the Carboniferous bituminous coals are coals of Alabama and among the lignite and sub-bituminous are the coals from Western USA. Some coals enriched in As in USA are as the following: Pennsylvanian bituminous coals of Alabama; Central Appalachian and Eastern Interior Province; Paleocene lignite of the Gulf Coast; Wyoming and South Dakota [26].

2.3.3 Model of Arsenic Occurrence in Coal

Among the arsenic forms ("residence") in coal, there are three dominant forms: pyritic, organic and arsenate. Locally some others as in Clay, arsenopyrite, etc., are also possible [26].

Pyrite has been considered to be a main carrier of arsenic [27], although arsenopyrite is another probable minor host. Correlation between arsenic and Sulfur was noted. In U.S.coals, even averaging does not mask an evident As–S_{pyr} relation [28]. The Term S_{pyr} represents the sulfur content in the form of pyrite. The relation of arsenic and S_{pyr} in U.S. coals is shown in Table 2-5 [29].

Microprobe investigations has also confirmed arsenic occurrence in pyrite. [26] Finkelman suggested that some of high-As pyrites (≥1% As) might contain microinclusions of arsenopyrite. Maximum As is noted in pyrites from brackish environments. Pyrites are extremely enriched in arsenic. At the same time, in the coals hosting the pyrites, even the highest average As-content is no more than 2 ppm, and highest individual is nearly 5 ppm. Thus, pyrite is the dominant concentrator and carrier of arsenic in these coals [26, 30].

Table 2-5 The relation of As and S_{pyr} in U.S. coals.

Sulfur in Pyrite (S_{pyr})	Geometric mean of As±standard deviation (ppm)
0-1	3.4±3.9
1-3	20.3±3.3
>3	42.7±3.7

Source: S.L.Coleman , L.J. Bragg, 1990, " Distribution and mode of occurrence of arsenic in coal. In: L.L.Chyi, C.L.Chou (Eds.)", Recent Advances in Coal Geochemistry, Geol.Soc. Amer. Spec. Pap. 248, pp. 13–26.

The second form of arsenic in coal is organic arsenic (As_{org}). Observed accumulation of the arsenic in sulphide phases (As_{sulf}) may result from diagenetic transformation of: As_{org} =>As_{sulf}. The indication on As_{org} presence may be obtained by means of direct (analyses of coal materials) or indirect methods (calculations from the analyses of density fractions or selective leaching of the coal) [31-34].

Studies show that arsenic is partly present as an arsenate [35]. Semiquantitative estimation of As in coal sites in USA by a complex procedure (selective leaching, SEM, X-ray and microprobe analyses) showed that 85% of the gross arsenic is associated with pyrite but some part is in the arsenate form as a result of an As-bearing pyrite oxidation process [36].

2.3.4 Factors Affecting Arsenic Distribution in Coal

There are several factors that can affect the distribution of arsenic in coal. It is strongly affected by the ash yield, the sulfur contents and more weakly by sample position in coal bed column [26]. Ash yield is the percentage of material remaining after a fuel is burned; that portion of a laboratory sample remaining after heating under standard conditions to constant weight; i.e., until all the combustible matter has been burned away. A positive correlation of As with ash yield may result from As-bearing sulphide content (usually, in the high-sulfur and low-ash coals); such correlation may indicate an As sulphide phase (As_{sulf}) domination. However, the correlation may also result from clay matter content, usually, in low-S coals. Negative correlation of As with ash or an As maximum at a medium ash yield may result from organic arsenic (As_{org}) species in coal or from non-As bearing minerals. As a result, the relations of As with ash yield are highly variable [26].

Data on the realations of As content to ash yield are rather numerous. For the mean data from all U.S. coals, the relationship “As in coal-ash yield” is observed in Table 2-6 [28]. From this table, the data show that the increase of ash contents leads to the

Table 2-6 The relation of arsenic and ash yield in U.S. coals.

Coal Category (% Ash)	Mean Ash Content (%)	Mean As Content (ppm)
Low-ash (0-8)	5.24	~4
Medium-ash (8-15)	10.87	~7
High-ash(>15)	23.2	~10

Source: R.B.Finkelman, L.J.Bragg, S.J.Tewalt, 1990, “Byproduct recovery from high-sulfur coals”, Processing and Utilization of High-Sulfur coals, Vol. 3, Elsevier, Amsterdam, pp. 89– 96.

increase of arsenic content. However, this does not imply the arsenic concentration is solely controlled by the terrigenous ash; the increase arsenic with ash increase seems to be dependent on a contribution to the ash from As-bearing sulphides [28]. For the information about the effect of position of coal sample within coal bed column, it is often limited and not generalized. There are several specific cases from U.S.A [26] and currently there is no generalized conclusion.

2.4 Arsenic in Fly Ash

Contents and residence sites of arsenic in fly ash were estimated by means of different approaches such as thermodynamic modeling and direct analyses of fly ashes and their size fractions.

2.4.1 Thermodynamic Modeling

The whole modeling process is demonstrated in the paper [26]. In the theory, both sulfide and arsenate arsenic must evaporate as As^o. However, in oxidizing milieu of the flue gases, As will rapidly be oxidized to stable As (+V) and later condensed as As_2O_5. In reality, the process is strongly complicated due to thermally stable $CaAsO_4$ formation. Overall, the reaction is the following:

$$As_2O_5(gas) + CaO(solid) \Rightarrow CaAsO_4(Solid) \quad \text{..... (2-3)}$$

In such a reaction, the arsenic is chemisorbed from the gas phase on to the fly ash surface. It is very clear this process will be strongly influenced by CaO content in the fly ash. In reality, the whole process is influenced by the cooling rate of flue gases [26]. The thermodynamically predicted $CaAsO_4$ formation may occur only through slow cooling of the flue gases. In realistic condition, thermodynamic equilibrium may not be reached and in this case, As partitioning in fly ash will be in accordance with its size: the finer the size, the greater the As content. Such partitioning is due to physi-sorption [37]. Both cases are observed as the equilibrium-like and kinetic-like distribution of arsenic in fly ash.

2.4.2 Influence of Arsenic Particle Size

It is well known that the kinds of coal, in increasing order of alteration, are lignite (brown coal--immature), sub-bituminous, bituminous, and anthracite (mature). The degree of alteration (or metamorphism) that occurs as a coal matures from peat to anthracite is referred to as the "rank" of the coal. Low-rank coals include lignite and sub-bituminous coals. These coals have lower energy content because they have low carbon content. They are lighter (earthier) and have higher moisture levels. As time, heat, and burial pressure all increase, the rank does as well. High-rank coals, including bituminous and anthracite coals, contain more carbon than lower-rank coals which results in a much higher energy content. They have a more vitreous (shiny) appearance and lower moisture content then lower-rank coals [38].

From the above reviews, arsenic in coal occurs in two different forms, which vary depending upon the rank of the coal. The relationships of the average arsenic concentration in fly ash dependent on coal rank are the following: for bituminous coals (n=26), the average concentration of arsenic is 219 (from 11 to 1385) ppm; for sub-bituminous coals (n=8), the average concentration is 19.1 (from 8 to 34) ppm; for lignite coals (n=5), the concentration is 54.4 (from 21 to 96) ppm [39]. Generally speaking, in bituminous coals, arsenic occurs in the mineral pyrite, where it substitutes for sulfur in the pyrite structure. In lower rank coals, arsenic occurs as a part of an oxygenated complex [40]. Under coal combustion flame conditions, both forms of arsenic can vaporize in the hot portions of the combustor. In this process, it may undergo several additional transformation processes as the post-combustion gases cool [41]. These processes include persistence as a vapor throughout the combustor and the air pollution control device, heterogeneous condensation on the surface of existing fly ash particles, dissolution in the aluminosilicate ash particles to form highly non-ideal solution, heterogeneous chemical reaction with compounds on the surface of existing fly ash particles and, ultimately, partition between the vapor phase and particulate fly ash [42].

It is well known that partitioning process leads to the enrichment of arsenic in the smallest particles [42]. Particles with diameters of ~0.5 *u*m are collected with the least efficiency in particulate collection devices such as electrostatic precipitators (ESPs) and baghouses which may increase the deposition of submicrometer-sized particles in the downwind environment and subsequent migration into the water table [43].

The relationship between arsenic concentration and ash particle size is an important factor in regard to determining component behavior [4]. The term "relative enrichments" (RE) was introduced to describe the observed behavior properly [44]. It is defined as the following equation (2-4):

$$\mathrm{RE} = \frac{\text{element concentration in ash}}{\text{element concentration in coal}} \times \frac{\text{ash content in coal}}{100} \times (\%) \quad \text{(2-4)}$$

It was found that arsenic is significantly concentrated in the smaller particles [44]. For example, the finest particles (PFA), RE = 5.53, and for coarsest particles, RE = 0.5. The preferential concentration on finer fly ash particles has been frequently observed [45].

There are two views that explain these phenomena [4]. The volatilization of arsenic was followed by condensation on the total available surface area, which is larger in the small particles and the calcium present in fly ash was the probable cause of a solid-gas surface reaction transformation mechanism that occurred under post-combustion conditions. This interaction of fly ash particles with arsenic vapor contributes to the final partitioning of arsenic. Although it is well established that fly ash particles do capture arsenic species, the nature of interaction between fly ash particles and arsenic is not well understood. Though it was reported that physical adsorption is not the mechanism between the fly ash and the arsenic at the post-combustion zone, further experimentation is needed to study the mechanism of arsenic-fly-ash reaction [4].

2.4.3 Effect of pH on Arsenic Oxidation-State Distribution

There are several references related to the discussion about the major form of arsenic in the fly ash. Although several experimental studies have reported the presence of As (+III) in coal ashes which may be due to the incomplete oxidation process [46], the major form of arsenic in the fly ash is As (+V) [46, 47].

Arsenic is subject to a variety of reactions in heterogeneous aqueous systems, including oxidation-reduction, sorption, complexation, and precipitation [4]. Oxidation of As (+III) to As (+V) is reported to be very slow at neutral pH values but faster in strongly alkaline or acid solutions with certain catalysts [48,49,50]. pH also affects the adsorption of both As (+III) and As (+V) on surface active solids [51, 52,53]. The solubility of several scarcely soluble metal arsenates is pH dependent [54]. Finally, As (+III) and As (+V) can form soluble complexes with Fe (+III) and the stability depends on the oxidation state of arsenic also depends on the pH [52]. It is reported that the increasing ionization of As (+V) with increasing pH and the decreasing availability of metal cations which can form insoluble compounds with arsenic tend to enhance the solubility of arsenic at high pH.

The close similarity between arsenate (As (+V)) and phosphate (P (+V)) suggests that the higher oxidation state of arsenic can form a wide variety and complexity of precipitated solids, one or more of which may control solubility of arsenic at high pH [55]. It is still uncertain about the reliability of some of the thermodynamic data for the simple metal arsenates. With the absence of thermodynamic data for more complex arsenic compounds, there will be no further consideration of solubility controls on arsenic in these ash leachates [55]. Leaching studies indicated considerable variability among fly ashes in the form and quantities of arsenic released initially from the solid phase, echoing the conclusion by Theis and Wirth [55] that studies based on work with only one or two fly ashes may have little general validity.

2.4.4 Leaching Behavior of Arsenic from Fly Ash

Several references discussed about the factors that can affect the leaching behavior of arsenic. The factors which influence the leaching of arsenic from fly ash include pH, calcium, magnesium, reducing or oxidizing conditions, solid to liquid ratio, leaching time, temperature etc [56, 57, 58, 59]. Several mechanisms were proposed to interpret arsenic interactions with fly ash and the surrounding environment. For example, It was reported that 78-97% of the total As can be removed from the fly ash by leaching with 0.5 N sulphuric acid in a 1 M sodium citrate solution at a pH of five [47]. It is also reported that some surface-active solids, such as amorphous iron oxyhydroxide, which have isoelectric points in the basic pH range [59], may be expected to readily adsorb anionic arsenic species when their sorbing surfaces are positively charged. In addition, specific adsorption of the neutral arsenious acid molecule on amorphous iron oxyhydroxide has recently been shown to be important at environmentally realistic concentrations [60]. Research also suggests that $H_2PO_4^-$ can displace arsenate in fly ash and increase arsenic concentration in leachates [61].

From above it is very clear that most studies focus on the pH value as the important factor of the leaching behavior in all the research initiatives. There are several specific researches on the pH value to the leaching behavior of arsenic from the fly ash. For all the researches, it is reported that with different types of fly ash, the pH value can affect the leaching behavior differently.

Generally speaking, fly ashes can broadly classified into two groups, Type F and Type C, as outlined in specification C-618 by the American Society for Testing and Materials in 1982 [62]. Type F ashes contain little calcium, considerable iron, are acidic-natured and have a combined SiO_2, Al_2O_3 and $Fe_2O_3 \geq 70$ wt%. By contrast, Type C ashes contain considerable calcium (commonly 20-30 wt% CaO) and are alkaline-natured with SiO_2, Al_2O_3 and $Fe_2O_3 \geq 50$ wt%. Most, but not all, fly ashes fall into one of these two broad categories, that is, acidic fly ash (Type F) or alkaline fly ash (Type C).

Generally speaking, for acidic fly ash (Type F), when pH is relatively neutral (pH from 4-7), the leaching behavior is not obvious. For acidic and alkaline conditions, the arsenic has the best removal at high fly ash concentrations; for alkaline fly ash (Type C), the arsenic removal behavior decreases with the increase of the pH value. The next several researches discussed about the details of arsenic leaching behavior.

Jianmin Wang, Tian Wang, and Joel G. Burken [47] had the experiment to prove the significant role of pH in the leaching of the arsenic. The coal they used is Type F with the following analytical results: SiO_2 (55.7%), Al_2O_3 (29.4%), Fe_2O_3 (4.6%), K_2O (2.3%), TiO_2 (1.5%), CaO (0.83%), MgO (0.79%), SO_3 (0.55%), Na_2O (0.32%), and P_2O_5 (0.11%). The total arsenic concentration in the fly ash was 48.1±0.5 μg/g. The experiment result chart is shown in Figure 2-4 [47].They conclude from the experiment that arsenic is released when pH is less than 3 or greater than 7, while in pH range between 3 and 7 very little arsenic is released. This can be explained with arsenate speciation analysis. When the pH is very low, (pH<2), the major arsenic species is H_3AsO_4, which does not have charge. It appears that the neutral arsenic molecules are not easily absorbed by ash surfaces. When pH is increased above 2, the total concentration of anionic arsenic species ($H_2AsO_4^-$ and $H_2AsO_4^{2-}$) is also increased. These anions can be easily and strongly adsorbed by the positively charged ash surfaces. When the pH is increased above pH 7, both ash surface and arsenic are negatively charged, which results in the arsenic release. In presence of calcium, when pH is increased, more arsenic is in the free arsenate form, which will form precipitate with calcium. If the pH is increased beyond 11, free cation concentration will be decreased due to the formation of metal hydroxides. Therefore, some precipitated arsenic can be dissolved due to the decrease of free cation concentration [47].

In the experiment, both As (+III) and As (+V) were detected in ash but the latter was present in much higher fraction [47]. Within the 4-12 pH range, most ash leachates of the principal inorganic arsenic species are oxyanions and oxyacids. As an anionic or

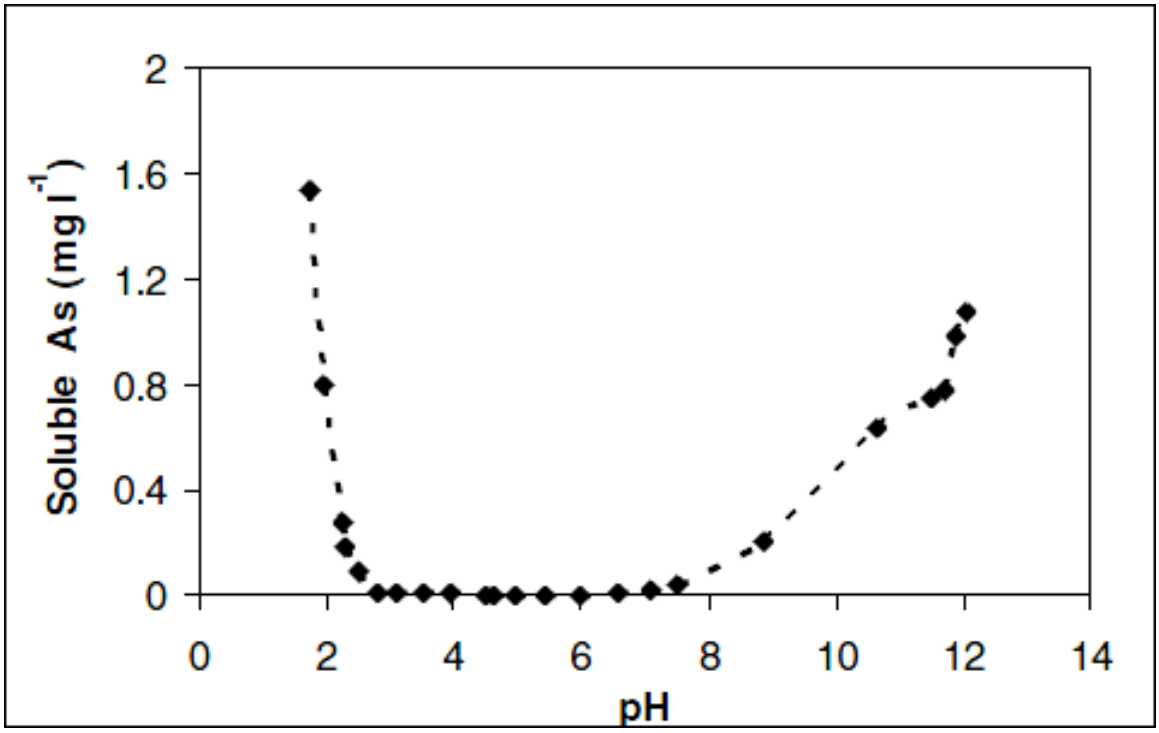


Figure 2-4 Batch leaching results for the raw Type F fly ash. Experimental conditions: Solid/Liquid=1:10; temperature=20-25°C; equilibration time = 24 hour.

Source: Jianmin Wang, Tian Wang, Joel G. Burken, Charles C.Chusuei, Heng Ban, Ken Ladwig, C.P.Huang, 2008, ”Adsorption of arsenic (V) onto fly ash: A speciation-based approach”, Chemosphere 72 (2008) 381-388.

neutral species, arsenic is more mobile in surface water and groundwater than most trace metal cations [47].

In other researches using the Type C fly ash, it was also noted that pH was important. Evan Diamadopoulos, Socrates Ioannidis and George P. Sakellaropoulos [63] had the research on the As (V) removal from fly ash aqueous solutions. From the experiment results, it is shown that the adsorption of arsenic (+V) on fly ash is, to a large extent, irreversible and pH dependent. They conclude that arsenic (+V) adsorbs strongly on fly ash. The equilibrium is practically achieved in less than 72 hours, while most of adsorption takes place in less than 24 hours; Equilibrium studies of As (+V) on fly ash show that arsenic adsorbs more strongly at pH 4 as opposed to pH 7 and pH 10. Complete removal of arsenic is possible at pH 4 at high fly ash concentrations; the maximum ash loading at pH 4 is 4 times as high at pH 7, and 3 times as high as at pH 10; Very little arsenic desorbs from fly ash at the same pH as the adsorption studies. This is more prominent at pH 4. This observation indicates that a large part of As (+V) adsorbs irreversibly on fly ash [63].

Besides the conclusions above, they also discussed about the possible adsorption mechanism as the following: There are electrostatic attraction (which gives rise to ion exchange with the counter-ions in the diffuse layer) and specific adsorption (surface complexation). The possible sites on the fly ash surface for specific adsorption at low pH include hydrous oxides of aluminum and iron. Surface complexation may occur when a proton from an un-dissociated arsenate ion forms a molecule of water with the hydroxyl group of the hydrous oxide followed by its displacement by the arsenate ion. The potential for surface complexation will depend on the protonation state of the arsenate ion and will be more favorable at lower pH. As pH increases, the ability to displace the hydroxyl groups from the hydrous oxides is reduced, since less arsenate ions are protonated. Removal of arsenic at high pH is primarily due to adsorption on calcium and magnesium oxides [63].

Another example using Type C fly ash is the research by David A. Grisafe, Ernest E.Angino, and Stephen M. Smith. They use Type C fly ash to study the leaching characterisitics of a high-calcium fly ash as a function of pH [62]. They use 4 different kinds of fly ash with different compositions as shown in Table 2-7 [62]. The experiment result is shown in Figure 2-5 [62]. Analyses for arsenic showed that the highest concentration occur in the leachate at pH 4.0 and decline with increasing pH. Concentration of arsenic exceeded the Environmental Protection Agency (EPA)'s toxicity criteria at pH 4.0. In near neutral pH, arsenic was below its toxicity levels. For pH higher than 7, the leaching behavior of arsenic is relatively negligible.

Besides the above researches, there are also several researches that have the opposite experiment results. One example is the research on mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems by Jerzy Jankowski, Colin R.Ward, David French and Sarah Groves [64]. They use two Type F fly ashes as FA15 and FA23; also, they use another two Type F fly ashes as FA16 and FA21. The pH for these four fly ashes is the following: 4.25, 4.84, 10.22 and 12.03. The detailed compositions of these four fly ashes are shown in Table 2-8 [64]. The study found out that for both acidic fly ashes (FA15 and FA23), the arsenic concentration increased with increasing pH values, and in both alkaline fly ashes (FA16 and FA21), the arsenic concentration also increased with increasing pH, but later in time the As concentration decreased. It is shown in Figure 2-6 [64]. This is an opposite experiment results compared to the first two researches. Usually, in alkaline fly ashes, the arsenic concentration increased with decreasing pH. The authors of this paper gives the following explanation that different processes are responsible for controlling As partitioning and As concentrations in alkaline fly ashes and acidic fly ashes.

It is thus possible that As in fly ash is present in great amounts in the silicate matrix and the rest is associated with iron rich glass phases, non-magnetic phases and non-silicates, or is accumulated on the surfaces of fine particles [64].

Table 2-7 Normalized chemical analyses of inorganic portion of fly ash samples.

	KP&L 38 (wt %)		KP&L 39 (wt %)		KP&L 40 (wt %)		Average	
	Size<5μ	Whole	Size<5μ	Whole	Size<5μ	Whole	Size<5μ	Whole
CaO	35.3	30.9	38.6	33.7	41.6	34.4	38.5	33.0
SiO_2	21.1	29.1	20.4	28.4	18.7	31.0	20.0	29.5
Al_2O_3	19.5	17.3	18.9	17.0	17.9	15.5	18.8	16.6
MgO	7.7	6.6	7.4	6.7	7.1	5.8	7.4	6.4
FeO	4.3	5.4	5.2	5.5	6.0	5.2	5.2	5.4
Na_2O	2.1	2.5	2.8	2.3	1.9	2.2	2.3	2.3
TiO_2	1.8	1.9	2.0	2.2	1.8	1.7	1.9	1.9
K_2O	0.4	0.4	0.2	0.2	0.3	0.3	0.3	0.3
SO_3	4.7	3.6	3.0	2.8	2.9	2.7	3.5	3.0
P_2O_5	3.2	2.4	1.5	1.2	1.8	1.3	2.2	1.6
Total	100.1	100.1	100.0	100.0	100.0	100.2	100.1	100.0

Source: David, A. Grisafe, Ernest E.Angino and Stephen M. Smith, 1988, “Leaching characteristics of a high-calcium fly ash as a function of pH: a potential source of selenium toxicity”. Applied geochemistry, vol.3, pp 601-608.

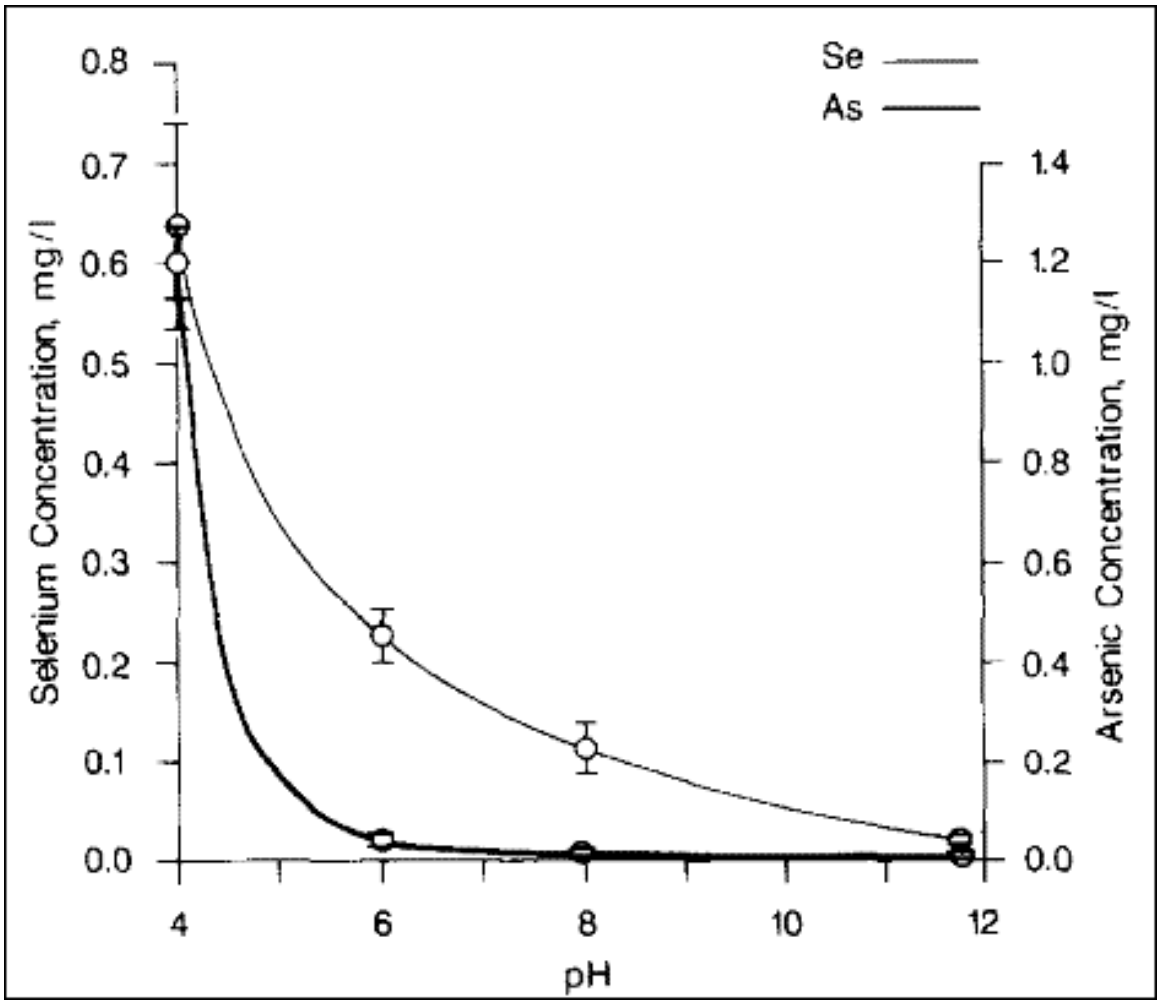


Figure 2-5 Arsenic and selenium concentrations in fly ash leachate as a function of pH. Vertical bars represent range of values.

Source: David, A. Grisafe, Ernest E.Angino and Stephen M. Smith, 1988, "Leaching characteristics of a high-calcium fly ash as a function of pH: a potential source of selenium toxicity". Applied geochemistry, vol.3, pp 601-608.

Table 2-8 Chemical analyses of fly ash samples. (wt %)

Element	FA15	FA16	FA21	FA23
SiO_2	52.3	48.8	64.9	66.0
TiO_2	3.7	2.4	1.4	1.3
Al_2O_3	19.2	27.8	17.0	27.6
Fe_2O_3	13.9	10.6	5.4	1.1
MgO	1.6	2.0	1.7	0.3
CaO	2.9	5.3	5.0	0.4
Na_2O	0.4	0.4	1.3	0.2
K_2O	1.4	1.1	2.9	2.9
P_2O_5	3.9	1.2	0.2	0.2
SO_3	0.6	0.3	0.2	0.1
Total	100.0	100.0	100.0	100.0

Source: Jerzy Jankowski, Colin R.Ward, David French and Sarah Groves, 2006, "mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems", Fuel 85 (2006) 243-256

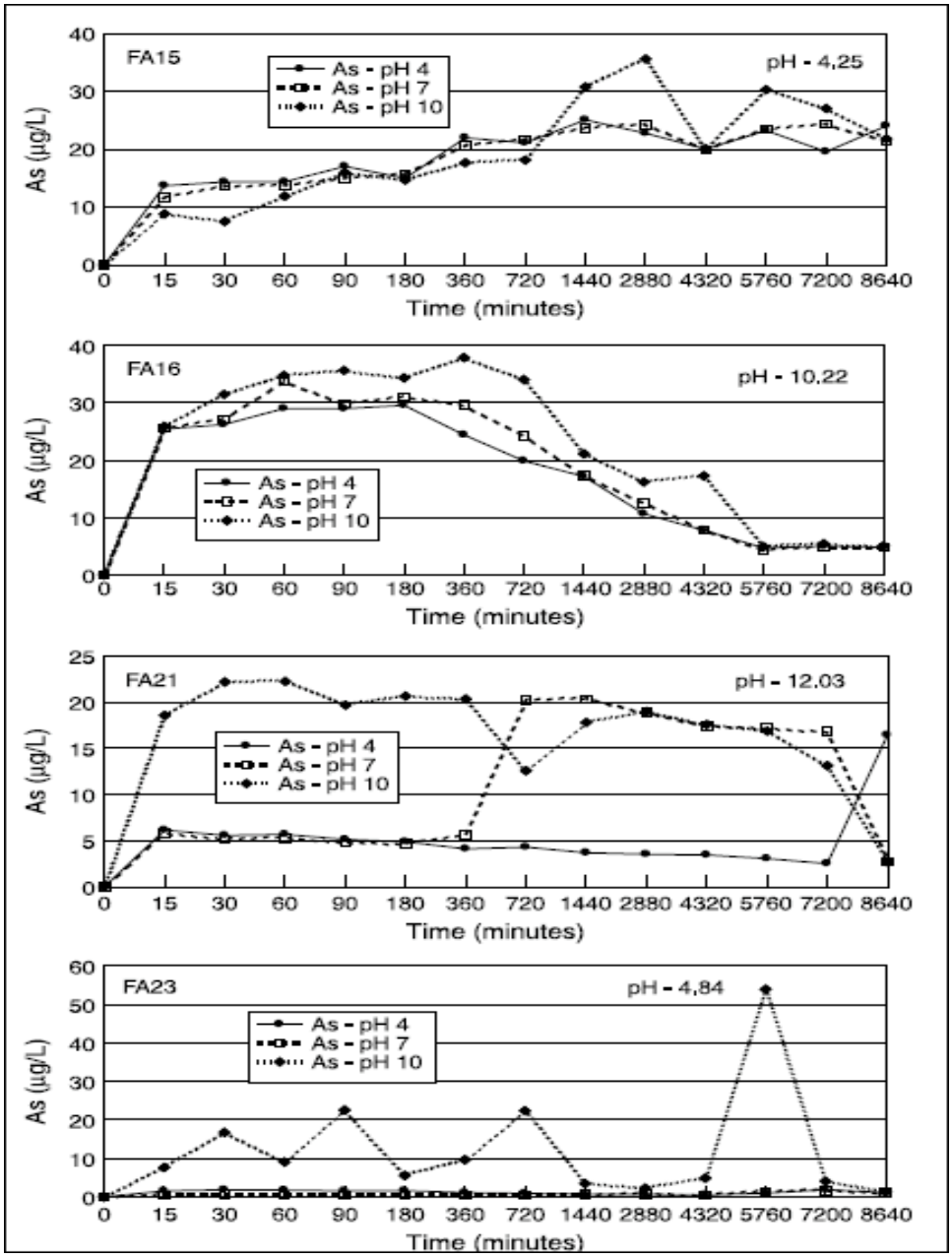


Figure 2-6 Changes of As concentrations with time during leaching tests in contact with fly ashes.

Source: Jerzy Jankowski, Colin R.Ward, David French and Sarah Groves, 2006, "mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems", Fuel 85 (2006) 243-256.

Because of As enrichment on the smaller particles, and also increased enrichment with increasing surface area, rapid mobilization of As occurred in early phases of leaching (FA16), and later, where there was no available As on the particle surfaces, the concentration decreased due to precipitation and/or sorption of As back into the solid phase [64]. Because pH controls As and its leach-ability, a low mobility is developed, where alkaline and neutral solutions are in contact with fly ash. However, if the As is present as oxyanions, it is more soluble in alkaline solutions. In alkaline fly ashes As solubility is low, but mobility is significantly higher than in acidic fly ashes, which is partly the case in the present study. Because the solubility of As (III) is nearly constant over a large pH range, solution of As (V) is probably responsible for the changes in As Total concentration and solution of As (V) with acidity/alkalinity changes is a major factor controlling the solubility and mobilization of As from fly ashes generally [64].

The last example is the research on the characterization of arsenic emissions from a coal-fired power plant [44]. They used 5 different types of fly ash with different compositions in Table 2-9 [44].

The experiment results showed that most of the arsenic is captured on the fly ashes; concern should be given to the leaching behavior and possible contamination [44]. The leaching results are shown in Table 2-10 [44]. Only data from EF-1 to EF-4 were assessed because there was an insufficient mass of PFA. These results help to assess the potential for arsenic that is contained in fly ash particles to migrate into the water supply after ground deposition downwind of the power plant. They conclude that among the various modes of occurrence, the water-extractable arsenic could migrate to water during the early stage of fly ash when contact with water. The readily exchangeable arsenic ions could be released under neutral conditions. These two are expected to influence the groundwater and soil environment [44].

Table 2-9 Concentrations of major components and loss on ignition (LOI) of fly ash.

Concentration (wt %)									
Fly ash	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	TiO_2	LOI (wt %)
EF-1	54.92	26.79	5.74	5.37	1.23	1.02	0.063	1.17	2.79
EF-2	57.91	31.03	8.42	5.84	1.24	0.99	0.076	1.33	3.57
EF-3	51.56	28.47	5.02	5.31	1.37	1.09	0.062	1.47	3.28
EF-4	56.81	26.01	5.87	5.39	1.12	0.78	0.063	1.44	3.85
PFA	59.31	25.7	4.17	5.27	1.77	1.46	0.058	1.39	2.01

Source: Xin Guo, Chu-Guang Zheng, Ming-Hou Xu, 2004, "Characterization of Arsenic Emissions from a Coal-Fired power Plant", Energy & Fuels 18, 1822-1826.

Table 2-10 Anaysis of the leachates obtained from fly ash.

Sample	Concentration (μg/g)		
	Water-extractables	Readily exchangeable ions	Carbonate-bound, surface oxide-bound ions
EF-1	0.021	0.46	1.44
EF-2	0.028	1.13	3.69
EF-3	0.058	1.08	6.16
EF-4	0.036	1.32	5.19

Source: Xin Guo, Chu-Guang Zheng, Ming-Hou Xu, 2004, "Characterization of Arsenic Emissions from a Coal-Fired power Plant", Energy & Fuels 18, 1822-1826.

In this paper it is reported that the arsenic in carbonate-bound, surface oxide-bound ions is sensitive to pH and has a tendency to dissolve into acid solution, which is the same tendency as the first two researches. The pH values of the leachate from fly ash were alkaline, in the pH range of 10.45-12.02, which prevents it from dissolving into the environment. These five kinds of fly ash are not the typical type C fly ash and the reason for this is not explained in the paper. Arsenic is partially soluble and some arsenic is expected to leach out of ash particles. It was reported that finer fly ash would release more arsenic into the environment [44].

Above all, most researches focused on the relationship between pH value and leaching behavior of arsenic. The results vary depending on different types of fly ash and pH conditions. In this thesis a proper simulation approach will be used in this study to properly understand and quantify the interactions between arsenic leaching behavior and pH value. It is also the purpose of this thesis to quantifiably model the arsenic distribution coefficient under different pH conditions from the simulation results.

Chapter 3

Materials and Methods

3.1 The Overview of Experimental Approach

Overall, the computational method is based on the OLI software simulation results. The first step is using OLI stream analyzers to analyze different types of fly ashes to predict different properties of the fly ashes. Here the main purpose is focused on the equilibrium pH value of the fly ash aqueous stream. Both Type F and Type C fly ash will be calculated in the study. Second, with the pH value obtained from the previous step calculation, use the "Composition Survey" function in OLI stream analyzers to simulate the leaching behavior of arsenic in aqueous system with different pH values. Finally, import the necessary data from the simulation results into the EXCEL spreadsheet model to speculate the possible distribution ratio of arsenic in the ash pond with the pH value as an input variable. As it shown above, the ultimate goal is to prove the OLI software as an practical alternative in predicting the arsenic leaching behavior and then find the perfect pH for the ash pond to have the optimized result for the distribution ratio of arsenic, that is, to maximize the concentration of arsenic in solid stream and minimize the arsenic concentration in effluent discharge in order to meet the future regulation.

3.2 OLI Stream Analyzers

OLI Stream Analyzer is one of the OLI Systems products designed for equilibrium simulation. It is OLI's simplest and clearest access to the electrolyte thermodynamic framework. The software features single point equilibrium calculations, multiple point survey calculations for trend analysis for temperature, pressure, pH and composition effects, and simple mix and separate capability. The calculations provide vapor, liquid, solid, and second liquid phase separations for a fully speciated model. Properties such as pH, ORP, viscosity, density, enthalpy as well as compositions are reported. Isothermal, adiabatic, bubble and dew point, set pH, vapor fraction and custom calculations are also available.

Water samples are accommodated as input and facilities for analysis recons OLI's MSEPUB databank for the Mixed Solvent Electrolyte (MSE) model is about 30% of the AQ model, with many priority systems completed. Redox, pseudo-components, private databanks and access to both the OLI AQ and MSE models are just some of the features that make this tool optimal for an in-depth electrolyte chemistry study.

In this study the main usage of this software is focused on the simulation of fly ash aqueous stream equilibrium pH value and the simulation of the leaching characteristics of arsenic in the ash pond. The main interface of this software is shown in Figure 3-1. The simulation of equilibrium pH value in fly ash aqueous stream is processed by the “single point” calculation in stream analyzers. The “single point” calculation can be processed in various conditions such as isothermal, isenthalpic, dew points, and bubble points etc. In this study all the single point is calculated under the isothermal condition. In this study, all the calculations are processed in the specification of temperature (T=298K), pressure (P=1 atm) and component inflows (varies with different coal fly ash). No other specifications are required.

The next step of simulation is the composition survey calculation of stream analyzers. As the single point calculation, the survey calculation is the combination of each single point calculations with different parameters. It can be processed in the conditions such as temperature, pressure, pH and composition. In this study all the survey calculations are processed in composition surveys. They are performed over a range of component compositions. Here the components are the acid and base titrants which can change the pH values of the aqueous system. In this study the titration pH range will be distributed from 2 to 14.

The composition survey consists of two steps: first, add the acid titrant to drop the pH from the fly ash pH calculated from single point calculation to the lower limit (pH=3). Second, use the base titrant to raise the pH to higher limit (pH=14).

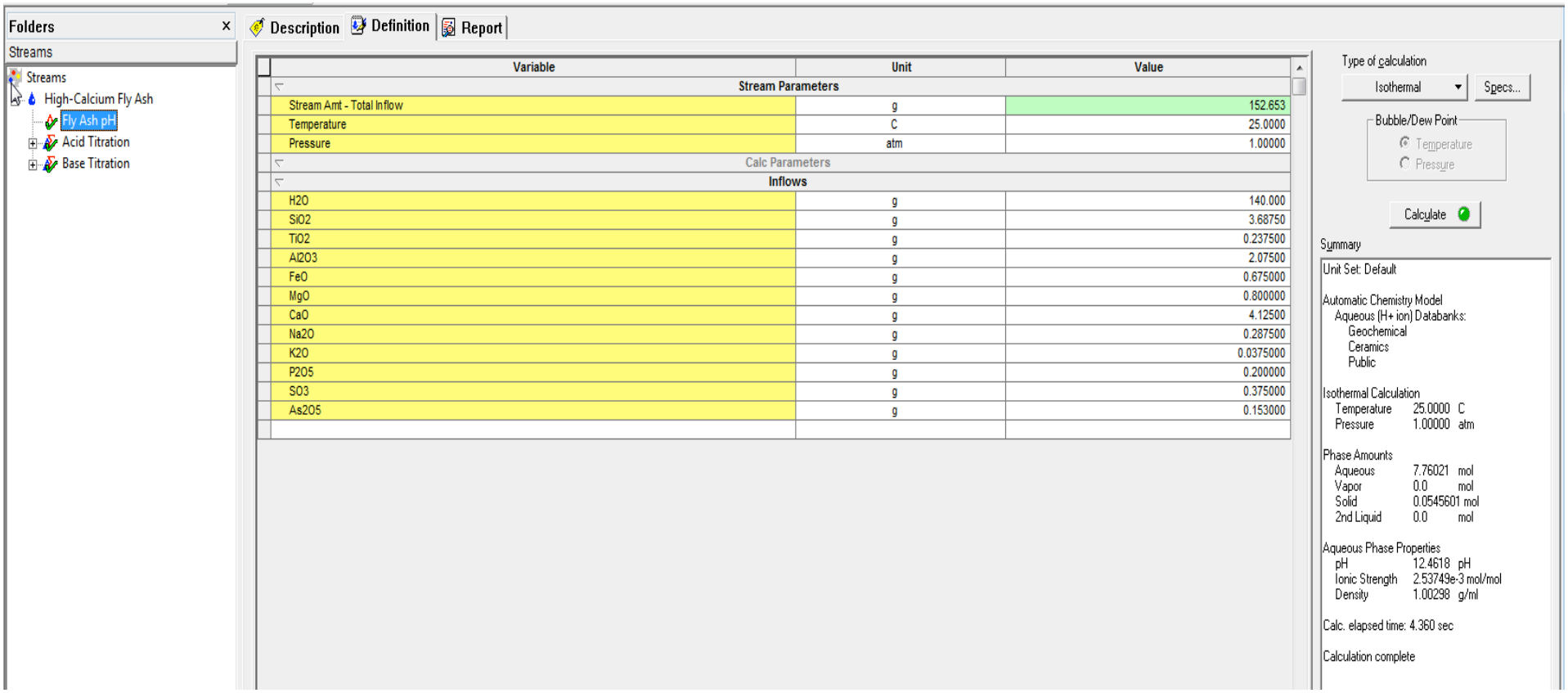


Figure 3-1 Software interface of OLI stream analyzer

After these two simulations the results can be combined together to get the whole results and charts about the leaching behavior of arsenic in aqueous systems. In this study, different kinds of fly ash (Type F and Type C) solutions will be used and the simulation results of arsenic leaching behavior of each solution will be compared with their experiment results.

3.3 EXCEL Spreadsheet Model for Arsenic Distribution

The main interface of the EXCEL Spreadsheet Model is shown in Figure 3-2. The whole model has four components-fly ash compositions, inflow parameters, simulation results and distribution coefficient (K_D) results with chart.

The fly ash composition section contains two parts: the components and the weight percent of each component. It includes all the common components that can exist in both types of fly ash. All data can be imported from the OLI stream analyzer calculation results. In the inflows parameters section here it includes the total mass of water, total mass of fly ash, total mass of the arsenic components in the fly ash solution, solid/liquid ratio and the acid/base titrant types. All the Data and parameters can also be imported from the report of stream analyzer.

In the simulation results section, the first component of this section is the pH of equilibrium fly ash solution obtained by the single point simulation. The second component of this section is the simulation results of composition survey which is the titration simulation for the fly ash solutions. This part lists all the possible output species of the simulation and the relative concentration of each component with different pH value. All the data need to be imported from the OLI stream analyzer calculation report. The last part of this spreadsheet is the distribution coefficient (K_D) results. In this study the K_D is defined by the definition of the ratio of arsenic in ash to the arsenic in water. It is shown in the following equation:

Spreadsheet Model for Arsenic Distribution

Fly Ash Composition	
Component	Percent by weight
CaO	33
SiO_2	29.5
Al_2O_3	16.6
Fe_2O_3	5.4
MgO	6.4
TiO_2	1.9
P_2O_5	1.6
Na_2O	2.3
K_2O	0.3
SO_3	3

Inflows Parameters	
Total Fly Ash Mass (g)	12.5
Total Water Mass (g)	140
Total As_2O_5 Mass (g)	0.153
Solid/Liquid Ratio	0.089285714
Acid Titrant	CH_3COOH
Base Titrant	NaOH

Distribution Coefficient (KD) Results			
pH	Aquesous (g)	Solid (g)	KD
2.99407604	1.86E-01	0.00E+00	0.00E+00
3.99639937	1.86E-01	0.00E+00	0.00E+00
4.99997259	1.86E-01	0.00E+00	0.00E+00
6.01841801	1.86E-01	0.00E+00	0.00E+00
6.9949166	1.86E-01	0.00E+00	0.00E+00
8.00070251	1.86E-01	0.00E+00	0.00E+00
9.00328755	1.86E-01	0.00E+00	0.00E+00
10.0196552	1.86E-01	0.00E+00	0.00E+00
11.0024123	5.08E-02	1.93E-01	4.25E+01
12.4618275	1.14E-02	2.49E-01	2.44E+02
13.0060489	1.61E-01	3.58E-02	2.49E+00
14.0018022	1.86E-01	0.00E+00	0.00E+00

Simulation Results

Single Point Calculation

			Fly Ash pH	12.4618			

Survey Calculation Aq=Aqueous Phase Sol=Solid Phase Unit:(mol)

pH	$As(OH)_2Cl_3(Aq)$	$FeAsO_4(Aq)$	$H_3AsO_4(Aq)$	$AsO_4(-3)(Aq)$	$Fe(HAsO_4)(+1)(Aq)$	$H_2AsO_4(-1)(Aq)$	$HAsO_4(-2)(Aq)$	$Ca_3(AsO_4)_2(Sol)$
2.99408	0.00E+00	0.00E+00	8.75E-06	3.75E-15	0.00E+00	5.41E-05	0.001268513	0
3.9964	0.00E+00	0.00E+00	1.07E-07	3.45E-14	0.00E+00	6.19E-06	0.001325067	0
4.99997	0.00E+00	0.00E+00	1.10E-09	3.33E-13	0.00E+00	6.33E-07	0.001330725	0
6.01842	0.00E+00	0.00E+00	1.02E-11	3.45E-12	0.00E+00	6.10E-08	0.001331299	0
6.99492	0.00E+00	0.00E+00	1.14E-13	3.25E-11	0.00E+00	6.48E-09	0.001331353	0
8.0007	0.00E+00	0.00E+00	1.35E-15	2.71E-10	0.00E+00	7.20E-10	0.001331359	0
9.00329	0.00E+00	0.00E+00	1.36E-17	2.67E-09	0.00E+00	7.23E-11	0.001331357	0
10.0197	0.00E+00	0.00E+00	1.27E-19	2.75E-08	0.00E+00	6.99E-12	0.001331332	0
11.0024	0.00E+00	0.00E+00	4.48E-22	5.05E-08	0.00E+00	2.39E-13	0.000362968	0.000484171
12.4618	0.00E+00	0.00E+00	1.66E-25	1.96E-07	0.00E+00	2.49E-15	8.15E-05	0.000624847
13.006	0.00E+00	0.00E+00	1.41E-25	1.17E-05	0.00E+00	8.45E-15	0.001139619	9.00E-05
14.0018	0.00E+00	0.00E+00	4.07E-28	0.000206807	0.00E+00	4.75E-16	0.001124553	0

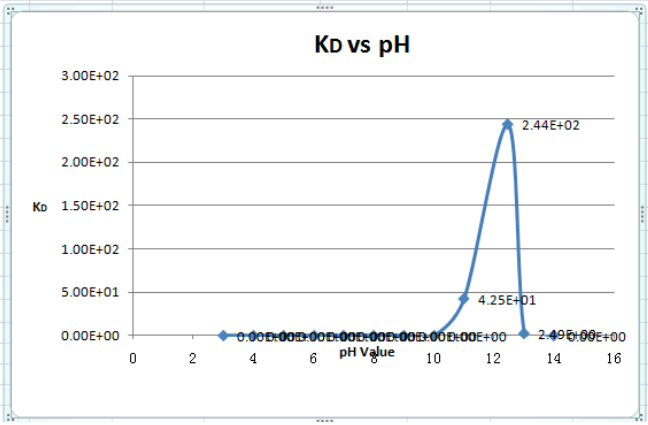


Figure 3-2 Main interface of EXCEL spreadsheet model

$$K_D = (\text{gram As/gram Ash}) / (\text{gram As/gram } H_2O) \quad \text{(3-1)}$$

By this definition and data obtained from the simulation results section, the spreadsheet can automatically calculate the arsenic mass both in aqueous phase and solid phase and finally output the distribution coefficient with different pH values. The output can also be observed from the chart in order to determine the best result of K_D by the variation of pH value.

Chapter 4

Results and Discussions

4.1 Single Point Calculation Results

4.1.1 Single Point Calculation Results and Experimental Results Comparison

Two cases will be simulated in this section. The first case is the comparison between predict results and actual results which are based on the results from the book" Air Pollution Engineering Manual" [65]. In the chapter seven of that book titled "combustion sources", the book listed fly ashes from 24 coal-fired plants with different characteristics. The details are shown in Table 4-1[65]. Within the 24 fly ashes, some of them are not listed with actual pH, therefore, the predicted result is not considered in this case.

Input all the data into the OLI stream analyzers and set the parameters as the following: solid to liquid (S/L) ratio is 1:10 (100g fly ash/1000g water), temperature at 25 °C (298K), pressure at 1 atm and the calculation type is isothermal calculation. The calculation process is shown in Figure 4-1. From this chart it is very clear to see the composition of the coal and the brief report of the calculation result such as pH value of the solution and phase amounts in the "definition" tag. The detailed report example is shown in Figure 4-2. From the report the details of the calculations are shown which include calculation summary, stream parameters, species outputs, molecular outputs, element outputs etc. The total 24 calculation results of the predicted pH value are also shown in Table 4-1. It is shown from the table that some of the predicted pH value is close to the equilibrium pH, however, some results are far from it. From the data it is clear that for all the fly ash equilibrium pH lower than 7, the predicted result is not accurate enough. It is also happened to some of the fly ash whose pH is greater than 7. From the definition of types of fly ash which is mentioned above, there are two types of fly ashes: type F (acidic) and type C (basic) and each have the typical component percentage.

Table 4-1 Fly ash characteristics from 24 coal-fired plants.

Fly Ash Type	Li_2O	Na_2O	K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	P_2O_5	SO_3	LOI	Soluble SO_4	Equilibrium pH	Predict pH
Monticello	0.02	0.49	0.99	2.2	9.7	3.4	20.4	60.5	1.9	0.08	0.44	0.29	0.48	9.81	7.76
Scholz HSFP	0.04	0.58	2.83	0.94	2.72	21.1	22.4	46.3	1.42	0.55	0.65	11.1	3.65	4.77	7.86
Brunner Island	0.06	0.32	2.7	0.93	2.33	11.7	28.5	49.6	1.53	0.71	0.36	6.1	3.1	4.26	7.81
IPP	0.03	2.1	1.46	2.68	10.72	6.1	19.6	53	1.1	0.61	1.56	0.64	1.95	10.68	8.30
Nixon	0.03	2.6	1.1	1.55	6	4.8	28.4	50.2	0.96	1.65	1.02	2.4	2	7.15	7.82
Shawnee Unit 5	0.06	0.4	2	0.84	1.8	4.5	31.5	53.8	2.7	0.19	0.34	6.3	1.83	4.38	7.70
Cameo	0.03	0.75	1.2	1.95	6.35	5	28.4	50.5	1.7	1.55	1.35	1.73	1.35	8.39	7.82
Harrington	0.01	1.55	0.4	6.05	29	6.3	18.8	30.5	1.25	1.45	2.6	0.53	3.15	11.05	11.78
Escalante	0.02	0.5	1.2	1.6	5.3	6.4	23.5	58.3	0.92	0.07	0.7	0.89	0.9	10	7.70
Arapahoe Unit 4	0.02	1.6	1.3	1.8	6.3	5.2	25.7	53.4	0.83	1.3	0.76	2.6	2	7.8	7.70
Arapahoe FFPP	0.02	2.8	1.3	1.6	4.9	4.1	26.4	55.5	1.1	1	0.78	1.8	1.5	7.27	7.70
Arapahoe FFPP 2	0.02	1.9	1.4	2.5	7.6	6.6	25.8	48	1	2	1.3	3.1	2.1	7.4	7.82
Arapahoe Ecolaire	0.02	1.4	1.3	2	6.2	5.7	26.3	52	0.92	1.6	0.71	3	1.8	7.4	7.82
Crane Unit 1	0.04	1.2	2.1	1.1	4.3	18.6	24.3	44.3	1.2	0.86	1.5	15.5	6.3	4.04	7.60
Comanche Ecolaire	0.01	1.2	0.18	6.6	35.9	5.3	18.8	21.8	1.8	2	3.3	0.55	4.2	11.4	12.81
Cherokee	0	0.57	1.1	1.8	5.6	4.6	28.2	52.1	1.5	1.7	0.95	1.6	1.07	N/A	7.70
Eraring	0.02	0.53	1.7	0.73	1.3	4.4	26.8	61.5	0.92	0.17	0.17	2	0.57	5.77	7.82
Tallawarra	0.02	0.11	1.2	0.52	0.95	4.9	20.1	70.5	0.84	0.19	0.13	3	0.65	5.45	7.82
TVA AFBC	0.03	1.33	1.05	1.85	34.67	10	11.4	22.4	0.53	0.27	15.78	11.1	16.58	11.47	11.7
Plant A CFBC															
Plant B CFBC	0.01	0.28	0.97	1.2	29.2	23.5	7.3	19.2	0.42	0.84	16.3	6.5	18.6	11.32	11.45
Nucla CFBC	0.03	0.18	0.93	0.81	16.4	3.8	23.9	45.1	1	0.04	5.8	8.8	6.6	11.4	9.01
EPRI High	0.61	0.4	0.65	0.7	31	4.1	7.4	15.2	0.35	0.24	39.1	5.8	43.6	10.3	11.94
Plant C Spray	0.02	1.7	1.2	1.3	12.2	4.4	18	48.4	0.91	0.05	10.6	2.5	12.1	10.4	7.86

Source: Wayne.R.Davis" Air Pollution Engineering Manual", 2nd edition, 2000, Wiley-Interscience Press.

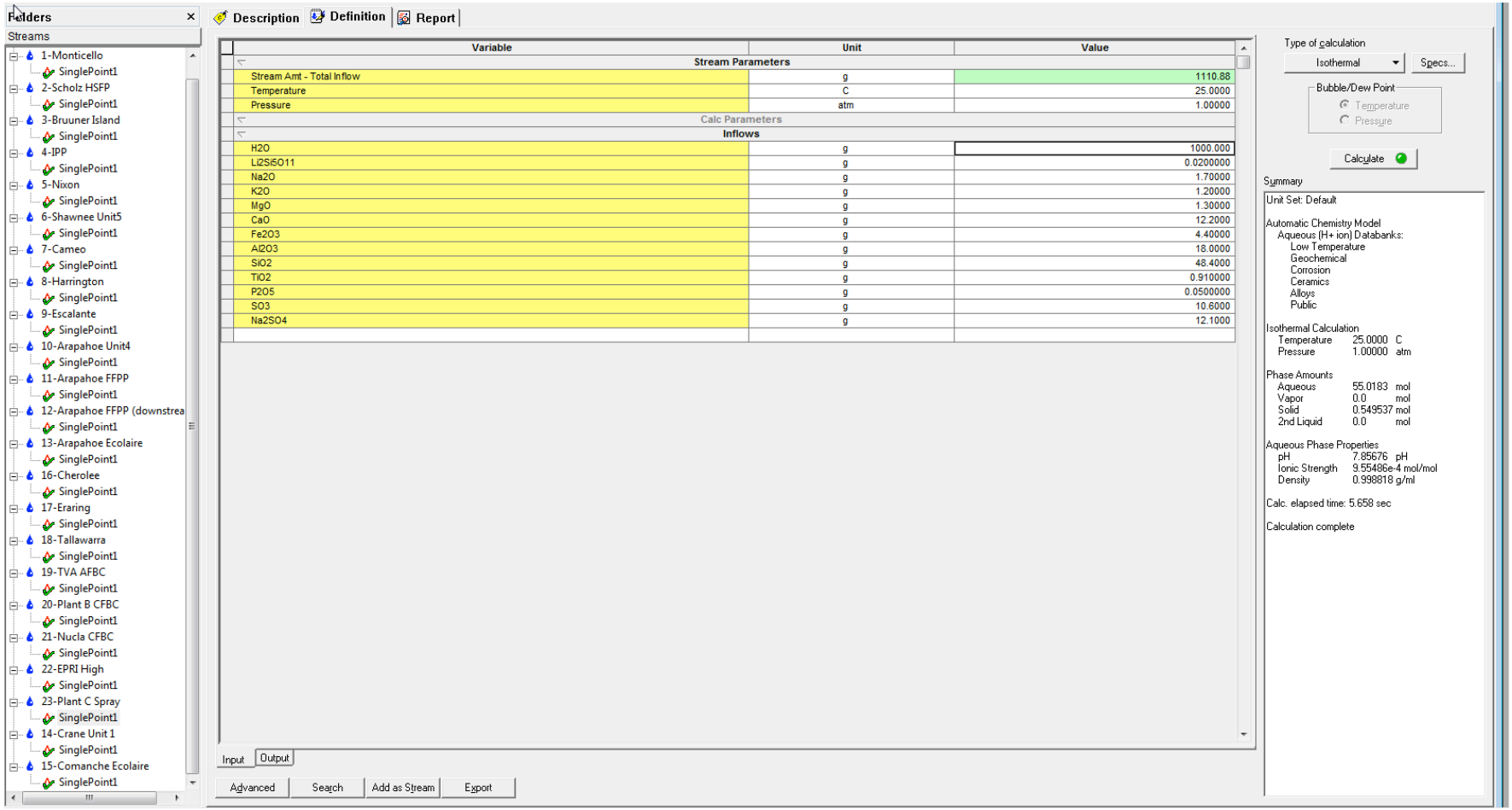


Figure 4-1 Single point calculation results from OLI stream analyzer

Stream Parameters
Row Filter Applied: Only Non Zero Values

Mixture Properties

Stream Amt - Total Inflow	1100.60	g
Temperature	298.150	K
Pressure	1.00000	atm

Aqueous Properties

pH	7.76323	pH
Ionic Strength	5.96556e-4	mol/mol
Osmotic Pressure	0.336630	atm
Electrical Cond, specific	1.34283e-3	1/(ohm-cm)
Electrical Cond, molar	0.885394	cm2/ohm-mol
Viscosity, absolute	0.896419	cP
Viscosity, relative	1.00640	cP/cP H2O

	Total	Aqueous	Vapor	Solid	2nd Liquid
		g/ml	g/ml	g/ml	g/ml
Density		0.998071	0.0	2.64126	0.0
	cal	cal	cal	cal	cal
Enthalpy	-4.14773e6	-3.76045e6	0.0	-3.87276e5	0.0
	cal/g K	cal/g K	cal/g K	cal/g K	cal/g K
Heat Capacity	0.0	0.0	0.0	0.0	0.0
		cal	cal	cal	cal
Gibbs Free Energy		0.0	0.0	0.0	0.0
		cal	cal	cal	cal
Gibbs Std State		0.0	0.0	0.0	0.0
		cal/K	cal/K	cal/K	cal/K
Entropy		0.0	0.0	0.0	0.0
		cal/K	cal/K	cal/K	cal/K
Entropy Std State		0.0	0.0	0.0	0.0

Species Output (True Species)
Row Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid	2nd Liquid
	mol	mol	mol	mol	n/a
H2O	55.0021	55.0021	0.0	0.0	0.0
SiO2	9.63901e-5	9.63901e-5	0.0	0.0	0.0
SO3	5.65549e-31	5.65549e-31	0.0	0.0	0.0
Al(OH)3	1.34369e-9	1.34369e-9	0.0	0.0	0.0
Al2Si2O5(OH)4	0.0121142	0.0	0.0	0.0121142	0.0
Ca2Mg5Si8O22(OH)2	0.0107364	0.0	0.0	0.0107364	0.0
Ca5(OH)(PO4)3	3.75662e-4	0.0	0.0	3.75662e-4	0.0
CaAl2Si3O10.3H2O	0.14175	0.0	0.0	0.14175	0.0
CaHPO4	5.79483e-8	5.79483e-8	0.0	0.0	0.0
CaSiO2(OH)2	7.35627e-10	7.35627e-10	0.0	0.0	0.0
CaSO4	5.3906e-4	5.3906e-4	0.0	0.0	0.0
Fe(OH)3	7.23218e-13	7.23218e-13	0.0	0.0	0.0
H0.33Fe2Al0.33Si3.67O10(OH)2	0.021291	0.0	0.0	0.021291	0.0

Figure 4-2 Detailed report of single point calculation

Type F ashes have a combined SiO_2, Al_2O_3 and $Fe_2O_3 \geq 70$ wt%. By contrast, Type C ashes contain considerable calcium wt%. (Commonly 20-30 wt% CaO) and are alkaline-natured with SiO_2, Al_2O_3 and $Fe_2O_3 \geq 50\%$. More details are shown in Table 4-2.

From Table 4-2 it is clear that for the possible Type C fly ashes, the simulation results are sufficiently close for use in this study to the actual experiment results and all the percentage errors are under 10%. For Type C fly ashes whose actual equilibrium pH is between 7 and 9, the predicted results are also reasonably close. The percentage errors for these fly ashes are all under 10%. For those of the fly ashes whose simulation results are not close to the actual equilibrium ones, it is also easy to separate the results into three groups. The percentage errors of all the fly ashes whose actual pH is below 5 are all above 60%. 6 fly ashes belong to this group. For the fly ashes whose actual pH is between 5 and 6, the error is dropped to 30%-45%. There are 2 fly ashes belong to this group. The last groups of fly ash which have the actual pH from 9.5 to 11.5 have the percentage error between 20%-30%.Overall, 11 fly ashes have the close simulation results and 11 fly ashes have the results which percentage error is above 20%.Therefore, it is clear to speculate the OLI stream analyzer can get accurate simulation results for all the Type C fly ash and some of the Type F fly ashes whose equilibrium pH is between 7 and 9.

From Table 4-2, it is also noted that CaO and Fe_2O_3 are the most important components to affect the overall pH of all the fly ashes. These two components have the opposite effect to the overall pH value of the fly ash solutions. For example, For all the fly ashes whose percentage error is bigger than 20%,if the fly ashes whose pH are below 5, the Fe_2O_3 component percentage are always higher than 10% and the CaO component percentage are lower than 5%. The percentage errors for these fly ashes are the highest. For the fly ashes whose pH is between 5and 6, the Fe_2O_3 percentage are lower than the first one and the percentage error drops to 30-40%. When the CaO component percentage is higher than the Fe_2O_3 while still under 17%, the percentage error drops to around 20%.

Table 4-2 Fly ash types and percentage error.

Fly Ash Type	CaO	Fe_2O_3	Al_2O_3	SiO_2	Equilibrium pH	Predict pH	Possible Fly Ash Type	Percentage Error (%)
Monticello	9.7	3.4	20.4	60.5	9.81	7.76	Type F	20.89
Scholz HSFP	2.72	21.1	22.4	46.3	4.77	7.86	Type F	64.77
Brunner Island	2.33	11.7	28.5	49.6	4.26	7.81	Type F	73.71
IPP	10.72	6.1	19.6	53	10.68	8.30	Type F	22.28
Nixon	6	4.8	28.4	50.2	7.15	7.82	Type F	9.37
Shawnee Unit 5	1.8	4.5	31.5	53.8	4.38	7.70	Type F	75.80
Cameo	6.35	5	28.4	50.5	8.39	7.82	Type F	6.79
Harrington	29	6.3	18.8	30.5	11.05	11.78	Type C	6.60
Escalante	5.3	6.4	23.5	58.3	10	7.70	Type F	23
Arapahoe Unit 4	6.3	5.2	25.7	53.4	7.8	7.70	Type F	1.28
Arapahoe FFPP	4.9	4.1	26.4	55.5	7.27	7.70	Type F	5.91
Arapahoe FFPP 2	7.6	6.6	25.8	48	7.4	7.82	Type F	5.68
Arapahoe Ecolaire	6.2	5.7	26.3	52	7.4	7.82	Type F	5.68
Crane Unit 1	4.3	18.6	24.3	44.3	4.04	7.60	Type F	78.22
Comanche Ecolaire	35.9	5.3	18.8	21.8	11.4	12.81	Type C	13.33
Cherokee	5.6	4.6	28.2	52.1	N/A	7.70	Type F	
Eraring	1.3	4.4	26.8	61.5	5.77	7.82	Type F	33.45
Tallawarra	0.95	4.9	20.1	70.5	5.45	7.82	Type F	41.28
TVA AFBC	34.67	10	11.4	22.4	11.47	11.7	Type C	2.01
Plant A CFBC								
Plant B CFBC	29.2	23.5	7.3	19.2	11.32	11.45	Type C	1.59
Nucla CFBC	16.4	3.8	23.9	45.1	11.4	9.01	Type F	20.96
EPRI High	31	4.1	7.4	15.2	10.3	11.94	Type C	7.77
Plant C Spray	12.2	4.4	18	48.4	10.4	7.86	Type F	28.17

These results are all for the fly ashes whose simulation results are not accurate enough compared to the equilibrium pH value. For those fly ashes who have the accurate results, the results can also divide into two cases: first, for the fly ash whose pH is between 7 and 9, it is clear that the component percentage of CaO and Fe_2O_3 are at the same level. The difference of CaO to Fe_2O_3 is always smaller than 2%. For example, the Cao component and Fe_2O_3 percentage are 6.35 and 5 respectively in the Cameo fly ash; it is also shown the same level of amounts in Nixon fly ash. Second, for all the Type C fly ashes, the results are clear: the Cao component is always higher than 20-25% and it is 3-4 times higher than the Fe_2O_3 and the simulation results are all very accurate. Therefore, the conclusion from Table 4-2 is very obvious: CaO and Fe_2O_3 affect significantly the overall pH for the fly ash. The overall pH increases with the increase of the CaO component percentage and the decrease of the Fe_2O_3 component percentage. For all the fly ashes that have the same level of percentage (percentage difference smaller than 2%) in CaO and Fe_2O_3 and all the Type C fly ashes whose CaO component are higher than 25% are 3-4 higher than the Fe_2O_3 component percentage, the OLI software simulation results are acceptable. However, for those fly ashes whose CaO component percentage is higher than the Fe_2O_3 while still under 17%, the percentage error starts to increase to 20-30%; when the Fe_2O_3 component percentage is higher than the CaO and still under 5%, the error increases to 30-40%; when the Fe_2O_3 component percentage is higher than 10% and 4-5 times than the CaO, the error increases to 70-80%.The detailed results are categorized and showed in Table 4-3.

From Table 4-3, it is easy to predict the validity of OLI stream analyzer from the composition percentage and equilibrium pH of the fly ash. Another example here is using the data from Table 2-9 to prove the above conclusions. The parameters are as the following : solid to liquid (S/L) ratio is 1:3:5 (39g fly ash/140g water), temperature at 25 °C (298K), pressure at 1 atm and the calculation type is isothermal calculation. CaO and Fe_2O_3 component percentage and equilibrium pH of each coal is shown in Table 4-4. The simulation results from OLI stream analyzers are shown in Figure 4-4 and Table 4-4.

Table 4-3 relationship among Fe_2O_3 & CaO component percentage, equilibrium pH and percentage errors.

Equilibrium pH	Fe_2O_3 & CaO Percentage (%)	Type of Fly Ash	Percentage Errors (%)	Example
pH<5	Fe_2O_3>10; Fe_2O_3>CaO (4-5times higher)	Type F	70-80	Scholz HSFP; Brunner Island; Crane Unit 1
5<pH<6	Fe_2O_3<5; Fe_2O_3>CaO	Type F	30-40	Eraring Tallawarra
7<pH<9	CaO>Fe_2O_3 (difference<2)	Type F	Under 10	Nixon; Cameo; Arapahoe FFPP; Arapahoe FFPP 2; Arapahoe Ecolaire;
9<pH<11.5	CaO>Fe_2O_3 CaO<17	Type F	20-30	Monticello; IPP; Plant C Spray; Nucla CFBC
11<pH<11.5	CaO>25 CaO>Fe_2O_3 (3-4 times higher)	Type C	Under 10	Harrington; TVA AFBC; Plant B CFBC; EPRI High

Table 4-4 Details from the calculation of fly ash in Table 2-8.

Fly Ash	Type	Fe_2O_3 Percentage (%)	CaO Percentage (%)	Equilibrium pH	Predict pH	Percentage Errors (%)
FA15	Type F	13.9	2.9	4.25	6.53	53.65
FA16	Type F	10.6	5.3	10.22	7.85	23.19
FA21	Type F	5.4	5.0	12.03	8.56	28.84
FA23	Type F	1.1	0.4	4.84	7.69	58.88

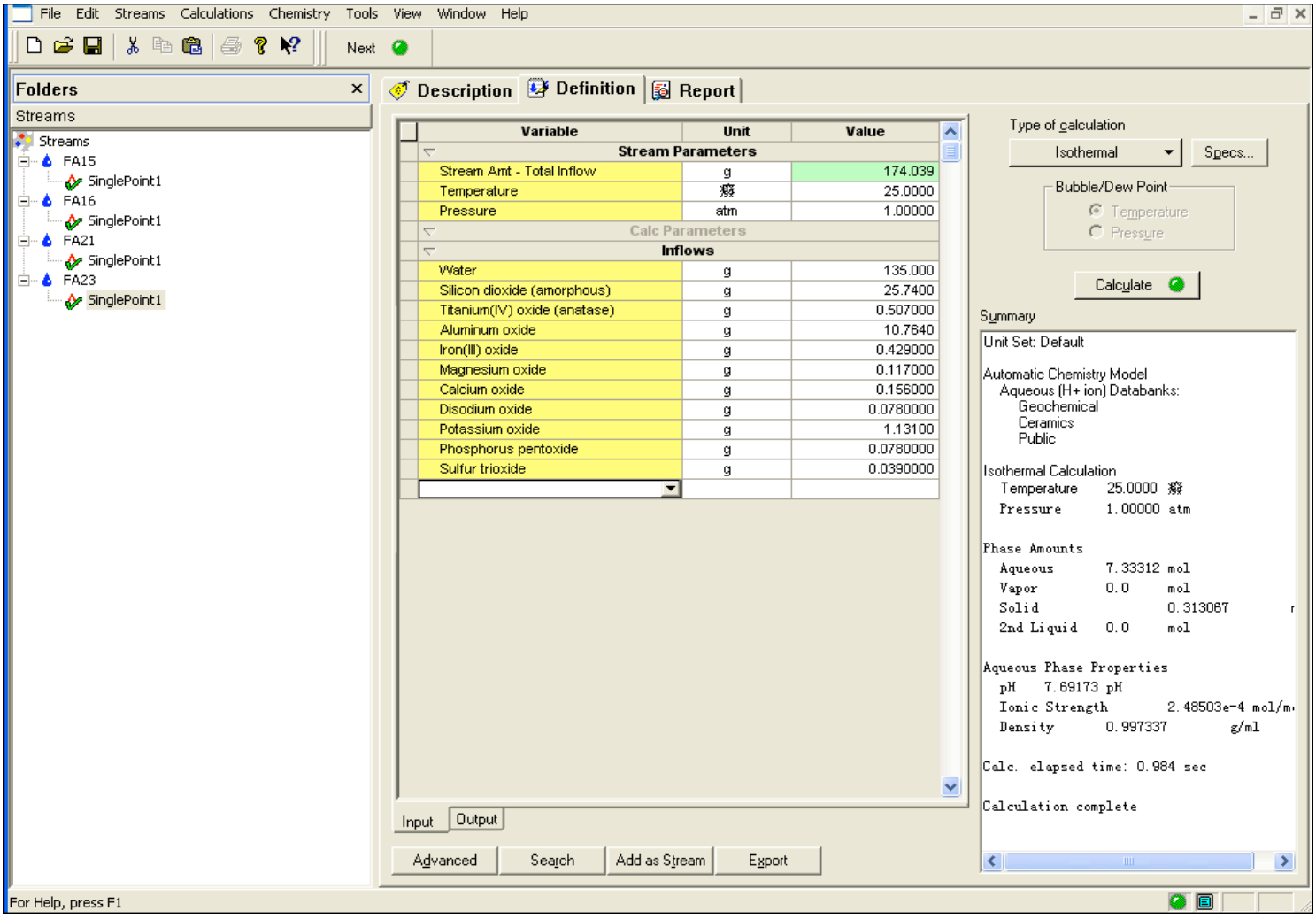


Figure 4-3 Calculations of fly ash in Table 2-8

It is clear to note that for the fly ash FA15 and FA23 whose equilibrium pH are below 5, the percentage error are higher than 50%; for the fly ash FA16 and FA23 whose pH are 10.22 and 12.03 respectively, the percentage errors are below 30%. This result proves the validity and possible percentage errors for the simulation above.

4.1.2 Relationship Between pH and Component Percentages of Fly Ash

As mentioned above, among all major components in most fly ashes are Fe_2O_3, CaO, SiO_2 and Al_2O_3. CaO and Fe_2O_3 have been proved effectively to affect the overall pH of fly ash. The overall pH increases with the increase of the CaO component percentage and the decrease of the Fe_2O_3 component percentage. The typical patterns are shown in Table 4-3 for 22 fly ashes and Table 4-4 for 4 fly ashes. However, there are also have several fly ash exceptions in the two tables. In Table 4-3, Shawnee Unit 5, Escalante and Comanche Ecolaire don't comply with the conclusions from Table 4-3. For Shawnee Unit 5, the Fe_2O_3 component percentage is below 5% however the percentage error is still higher 70% which does not follow the second case in Table 4-3. For Escalante, even though the Fe_2O_3 component percentage is higher than CaO the pH is higher than 7. For Comanche Ecolaire, it follows the last case in Table 4-3 while with a higher percentage error. In Table 4-4, Fe_2O_3 percentage is higher than CaO percentage in FA16 while still has a overall pH higher than 7; FA21 also has the same pattern. FA23 does not follow the conditions in the first case in Table 4-3.

The reasons for these exceptions could be various. First, each experiment conditions are different from each other. For each experiment, the stirring time and residue time for the fly ash solutions are different. What's more, the equipment and reagents used in each experiment are different from each other which could be partially the reason for the measurement errors. This could also explain the difference between actual pH and predict pH because the experiment conditions used in OLI stream analyzers are not exactly the same as in each experiment. For example, in each experiment, stirring time and residue time need to be considered. Typically, all the

solutions needed to wait at least 24 hours to measure the pH and in the software this factor is not included in the simulation due to the limit of the simulation process. Second, although the Fe_2O_3 and CaO are considered to be the major components affecting the pH, other components still need to be considered to contribute to the difference of pH. It is also possible that the components not mentioned in the research could affect the overall pH of the fly ash. For the OLI software, due to the limit of the software, it is hard to look over or modify the inside calculation mechanism, which could also be possible for the discrepancy of the predict pH. This point is also proved by the technical support from OLI Systems. Nevertheless, most of the fly ashes could follow the typical patterns and therefore the validity for OLI stream analyzers can be proved for the specific fly ashes as mentioned above.

4.2 Type C Fly Ash Composition Survey Calculation

As mentioned above, after the first step single point calculation, the software can give out the equilibrium fly ash solution s' pH values. Then use the acid and base titrants separately to change the pH from 3 to 14 to simulate the titration to predict the arsenic leaching behavior by the effect of pH value. Two kinds of Type C fly ashes will be used in the simulation and comparisons between simulation results and actual experimental results will be provided.

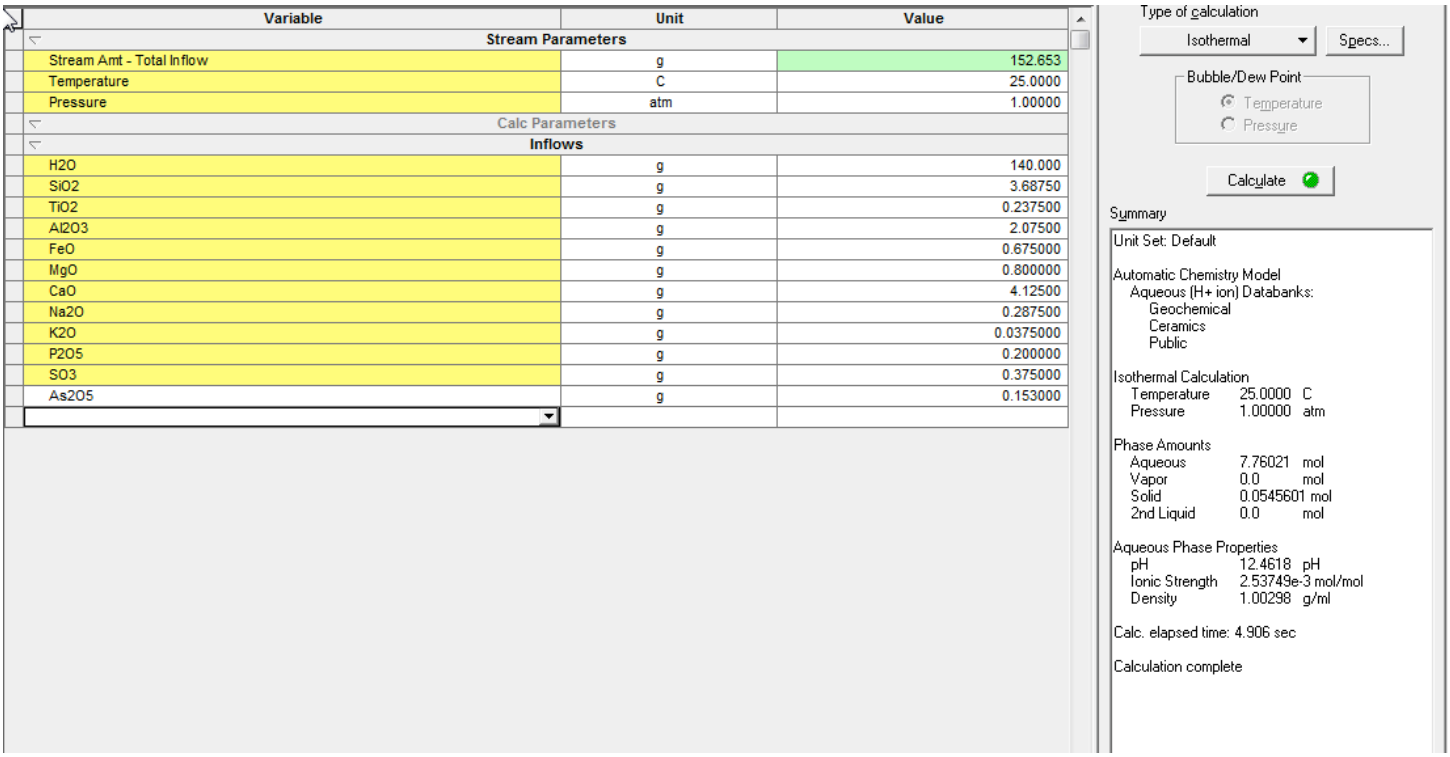
4.2.1 High-calcium Fly Ash Leaching Behavior Simulation

This Simulation is based on the study of leaching characteristics of a high-calcium fly ash as a function of pH value by David A. Grisafe, Ernest E.Angino and Stephen M.Smith [62]. The Fly ash used in this study is the typical Type C fly ashes. The major components weight percent of the fly ash, the inflow parameters are shown in Table 4-5. The component details are also shown in Figure 4-4. In the previous literature review section it is mentioned the dominant form of As in fly ash solutions is in (+V) [61], all the the arsenic added into the solution in the thesis is in the form of As_2O_5 and the amount can be converted from the experiment results in the paper.

Table 4-5 Major components weight percent of fly ash and inflow parameters

Inflow Parameters			Component by Weight Percent (%)									
Fly Ash Mass (g)	Water Mass(g)	As_2O_5 Mass (g)	CaO	SiO_2	Al_2O_3	FeO	MgO	TiO_2	P_2O_5	Na_2O	K_2O	SO_3
12.5	140	0.153	33.0	29.5	16.6	5.4	6.4	1.9	1.6	2.3	0.3	3.0

Source: David, A. Grisafe, Ernest E.Angino and Stephen M. Smith, 1988, "Leaching characteristics of a high-calcium fly ash as a function of pH: a potential source of selenium toxicity". Applied geochemistry, vol.3, pp 601-608.



Variable	Unit	Value
Stream Parameters		
Stream Amt - Total Inflow	g	152.653
Temperature	C	25.0000
Pressure	atm	1.00000
Calc Parameters		
Inflows		
H2O	g	140.000
SiO2	g	3.68750
TiO2	g	0.237500
Al2O3	g	2.07500
FeO	g	0.675000
MgO	g	0.800000
CaO	g	4.12500
Na2O	g	0.287500
K2O	g	0.0375000
P2O5	g	0.200000
SO3	g	0.375000
As2O5	g	0.153000

Figure 4-4 Component weight percent and fly ash pH simulation results

It is needed to be mention here that in the original study the stirring hours at each pH value is 24h period. The effect of stirring hours to the pH value is not included in the simulation.

From Figure 4-4 it is noted that the fly ash pH is 12.4618. After the first step, two composition surveys will be processed respectively. Here in the study the titrants used are acetic acid (CH_3COOH) and sodium hydroxide (NaOH). The species output section from the calculation report is shown in Table 4-6. It can be concluded from the table that the dominant As form in aqueous phase is $H_2AsO_4^{-1}$ and $HAsO_4^{-2}$ and the solid phase of Arsenic is in the form of $Ca_3(AsO_4)_2$. The concentrations of the dominant As forms in the titrations with the effect of pH is shown in Figure 4-5 and 4-6. After importing all the simulation results into spreadsheet model, the distribution coefficient with the effect of pH is shown in Figure 4-7.

It is clearly showed in Figures 4-5 that the concentration of arsenic in solid form reaches the maximum at the equilibrium fly ash pH where the concentrations of all aqueous arsenic forms reach the minimum and the concentration of arsenic in aqueous form is proved to show a general trend of decreasing solubility with increasing pH value. This conclusion can be also proved by Figure 2-5. In Figure 4-6, however, the concentration of all dominant components has a different trend. The solid phase of the arsenic compound decreases with increasing pH and the liquid phase of arsenic- AsO_4^{-3} increases when pH rises to 14. For the distribution coefficient, from Figure 4-7, the optimum value could be reached at the equilibrium fly ash pH to get the maximum concentration of arsenic in insoluble forms and minimum concentration in soluble forms.

4.2.2 As (V) Removal Process from Fly Ash Simulation

Another study using type C fly ash is the research on the As (V) removal process from aqueous solutions by fly ash by Evan Diamadopoulos, Socrates Ioannidis and George P. SakeLlaropoulos [61].

Table 4-6 Simulation results and concentrations of dominant As forms

Simulation Results								
Single Point Calculation								
Fly Ash pH=12.4618								
Survey Calculation Aq=Aqueous Phase Sol=Solid Phase Unit:(mol)								
pH	$As(OH)_2Cl_3$ (Aq)	$FeAsO_4$ (Aq)	H_3AsO_4 (Aq)	AsO_4^{-3} (Aq)	$Fe(HAsO_4)^{+1}$ (Aq)	$H_2AsO_4^{-1}$ (Aq)	$HAsO_4^{-2}$ (Aq)	$Ca_3(AsO_4)^2$ (Sol)
2.99408	0.00E+00	0.00E+00	8.75E-06	3.75E-15	0.00E+00	5.41E-05	0.001268513	0
3.9964	0.00E+00	0.00E+00	1.07E-07	3.45E-14	0.00E+00	6.19E-06	0.001325067	0
4.99997	0.00E+00	0.00E+00	1.10E-09	3.33E-13	0.00E+00	6.33E-07	0.001330725	0
6.01842	0.00E+00	0.00E+00	1.02E-11	3.45E-12	0.00E+00	6.10E-08	0.001331299	0
6.99492	0.00E+00	0.00E+00	1.14E-13	3.25E-11	0.00E+00	6.48E-09	0.001331353	0
8.0007	0.00E+00	0.00E+00	1.35E-15	2.71E-10	0.00E+00	7.20E-10	0.001331359	0
9.00329	0.00E+00	0.00E+00	1.36E-17	2.67E-09	0.00E+00	7.23E-11	0.001331357	0
10.0197	0.00E+00	0.00E+00	1.27E-19	2.75E-08	0.00E+00	6.99E-12	0.001331332	0
11.0024	0.00E+00	0.00E+00	4.48E-22	5.05E-08	0.00E+00	2.39E-13	0.000362968	0.000484171
12.4618	0.00E+00	0.00E+00	1.66E-25	1.96E-07	0.00E+00	2.49E-15	8.15E-05	0.000624847
13.006	0.00E+00	0.00E+00	1.41E-25	1.17E-05	0.00E+00	8.45E-15	0.001139619	9.00E-05
14.0018	0.00E+00	0.00E+00	4.07E-28	0.000206807	0.00E+00	4.75E-16	0.001124553	0

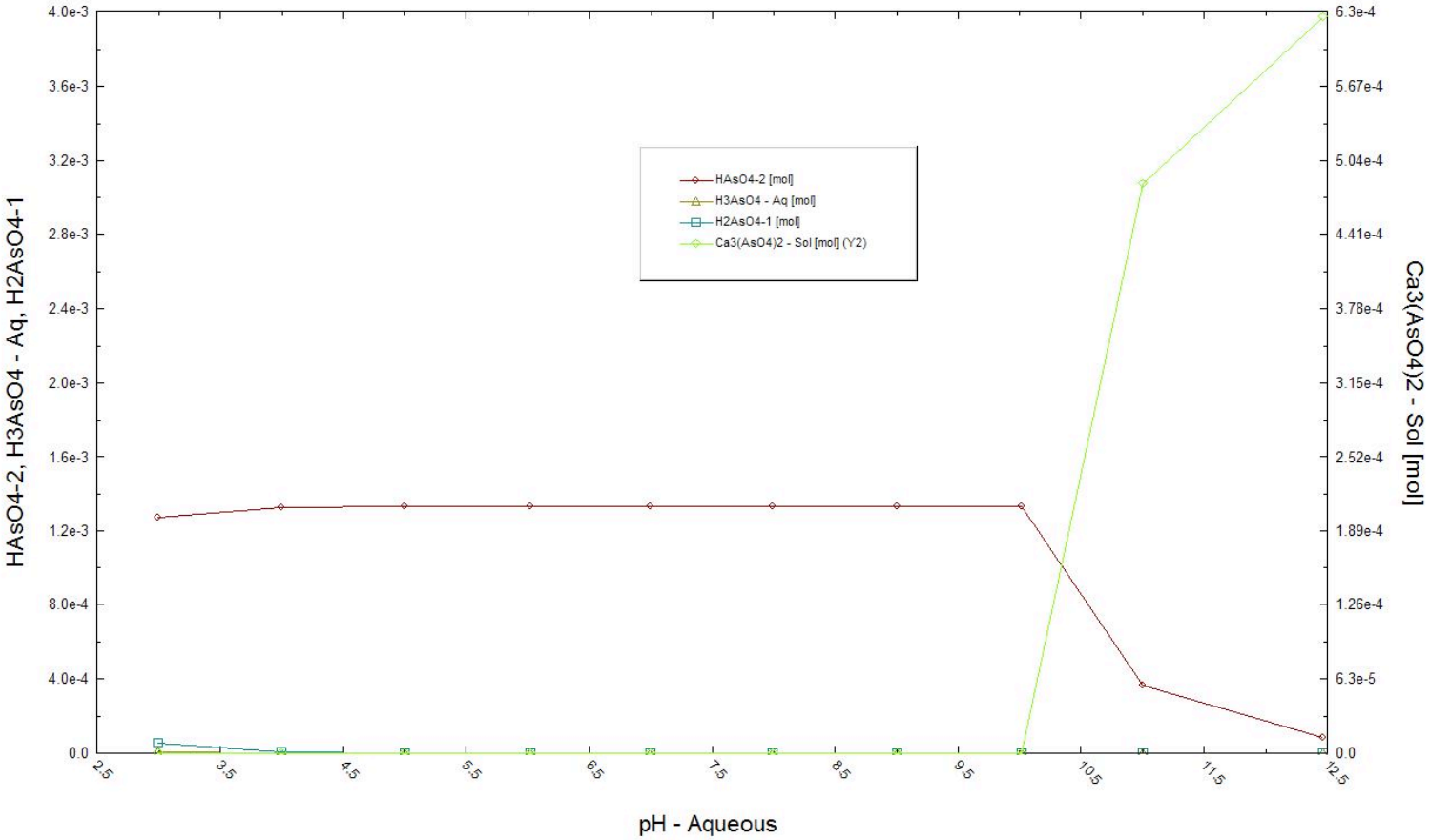


Figure 4-5 Concentrations of dominant As forms with the effect of pH in acid titration

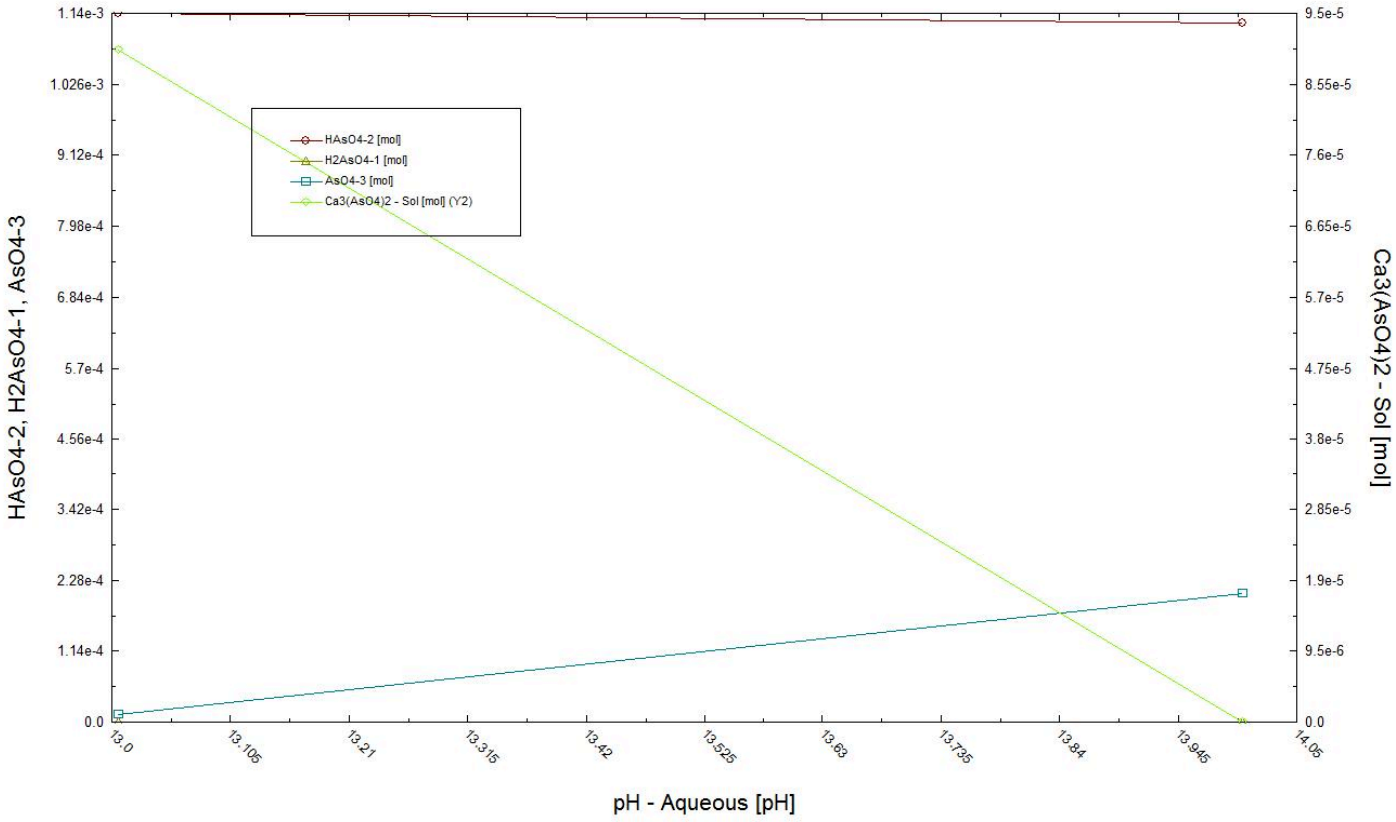


Figure 4-6 Concentrations of dominant As forms with the effect of pH in base titration

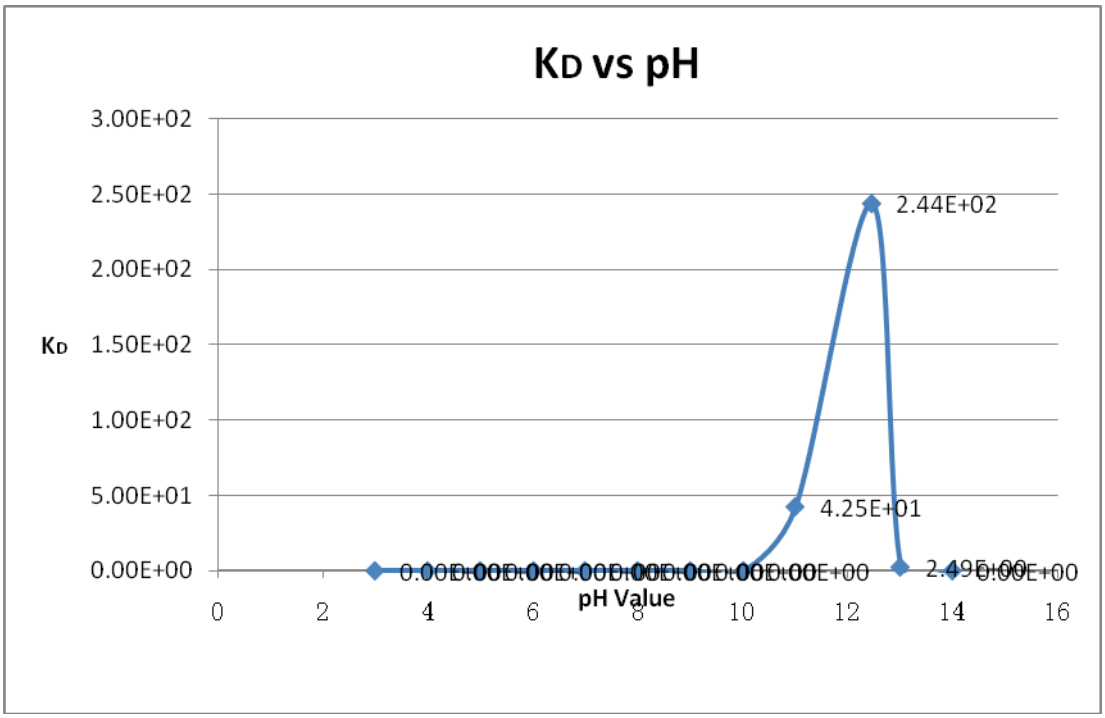


Figure 4-7 Distribution coefficient (K_D) vs pH value

As the previous study, the major components weight percent of the fly ash, the inflow parameters are shown in Table 4-7. In this study the stirring time is not illustrated. Similarly to the previous study, the simulation results are shown in Table 4-8. Figure 4-8, Figure 4-9 and Figure 4-10 are the concentration of dominant as forms in acid/base titration and the distribution coefficient variation with the increase of pH. Compared to the previous study, we can see the great similarity in both cases which all proved the arsenic adsorption/desorption behavior is pH dependent for Type C fly ash. From the results, the pH condition is in equilibrium fly ash pH which gives the maximum solid arsenic compound concentrations and the minimum liquid arsenic compound concentrations. The reason for this trend is presumably due to that the formation of insoluble compounds are mainly caused by the high weight percent of CaO in Type C fly ash. It is proved in the previous study that with the low-lime Type F ashes the tendency to form such compounds was minimized. It can also be concluded from Table 4-8 that the metal ions can be leached from fly ash and the mobility of such ions is greatly influenced by the pH. Although the amount of arsenic in the experiment is pretty tiny; however, for the coal-combustion power plant the total amount of arsenic could be enormous and therefore the metal ions will be precipitated with the increase of pH.

4.3 Type F Fly Ash Composition Survey Calculation

Compared to Type C fly ash, the main difference of type F fly ash is the weight percent of CaO. Mostly in type F fly ash the weight percent of CaO is limited, under 5%. Therefore, in the simulation the dominant arsenic form-$Ca_3(AsO_4)_2$ will not exist and all the arsenic will exist in aqueous form. In this case, the removal of arsenic is mainly caused by the adsorption to fly ash particles. As mentioned in the literature review, the adsorption of arsenic can be affected by various factors and in the simulation the main goal is to predict the concentrations of the dominant aqueous arsenic form with the effect of pH.

Table 4-7 Major components weight percent of fly ash and inflow parameters

Inflow Parameters			Component by Weight Percent (%)									
Fly Ash Mass (g)	Water Mass(g)	As_2O_5 Mass (g)	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	P_2O_5	Na_2O	K_2O	SO_3
10	150	0.075	36.5	25.1	10.3	7.6	5.2	0.9	0.02	0	0	0

Source: Evan Diamadopoulos, Socrates Ioannidis and George P. SakeLlaropoulos, "As (V) removal from aqueous solutions by fly ash", Water Resources, vol27, No12, pp 1773-1777, 1993.

Table 4-8 Simulation results and concentrations of dominant As forms

Simulation Results								
Single Point Calculation								
Fly Ash pH=12.3842								
Survey Calculation Aq=Aqueous Phase Sol=Solid Phase Unit:(mol)								
pH	$As(OH)_2Cl_3$ (Aq)	$FeAsO_4$ (Aq)	H_3AsO_4 (Aq)	AsO_4^{-3} (Aq)	$Fe(HAsO_4)^{+1}$ (Aq)	$H_2AsO_4^{-1}$ (Aq)	$HAsO_4^{-2}$ (Aq)	$Ca_3(AsO_4)^2$ (Sol)
3.05505	1.58E-20	9.16E-25	9.05E-07	7.22E-15	3.37E-12	7.81E-06	0.000643913	0
4.0062	2.17E-25	1.29E-26	1.29E-08	6.21E-14	5.13E-15	9.26E-07	0.000651688	0
4.97035	3.28E-30	1.53E-28	1.53E-10	5.72E-13	6.58E-18	1.01E-07	0.000652526	0
5.4475	1.35E-32	1.70E-29	1.70E-11	1.72E-12	2.44E-19	3.36E-08	0.000652594	0
7.00279	9.10E-41	1.79E-32	1.87E-14	5.22E-11	6.38E-24	1.11E-09	0.000652626	0
8.00286	2.31E-46	1.59E-34	2.75E-16	3.88E-10	4.97E-27	1.59E-10	0.000652627	0
9.00219	2.32E-51	1.60E-37	2.76E-18	3.87E-09	5.00E-31	1.59E-11	0.000652623	0
10.0012	1.84E-56	2.47E-40	2.95E-20	3.65E-08	7.55E-35	1.69E-12	0.000652591	0
10.9995	2.56E-62	7.78E-43	9.58E-23	8.36E-08	2.25E-38	5.40E-14	0.000177285	0.00023763
12.3842	0	3.92E-45	5.29E-25	1.47E-07	2.73E-42	5.82E-15	0.000117311	0.000267584
13.0023	0	1.17E-44	1.07E-25	5.05E-06	2.19E-42	5.82E-15	0.000647573	0
14.0084	0	2.30E-47	2.01E-28	0.000100294	6.75E-46	2.35E-16	0.000552333	0

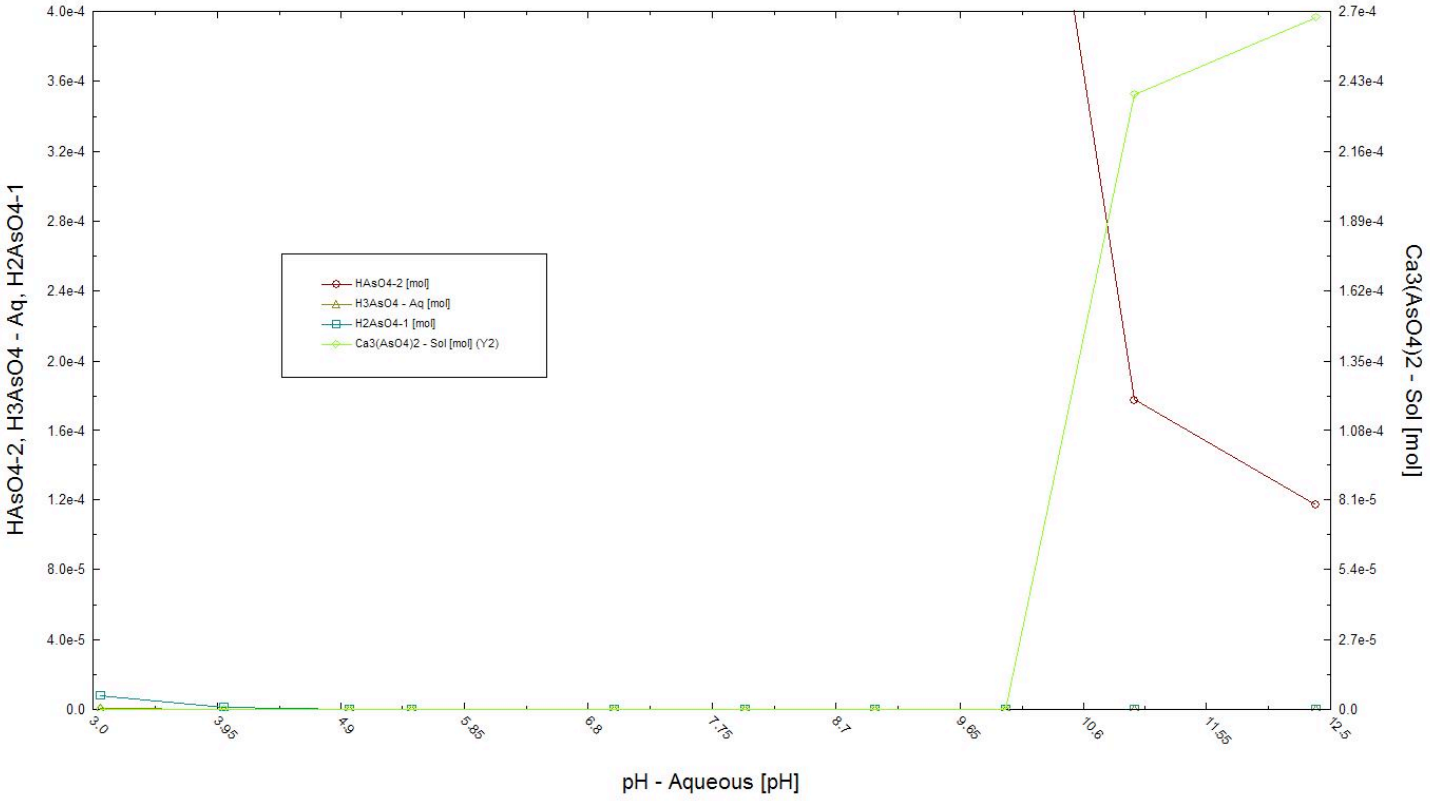


Figure 4-8 Concentrations of dominant As forms with the effect of pH in acid titration

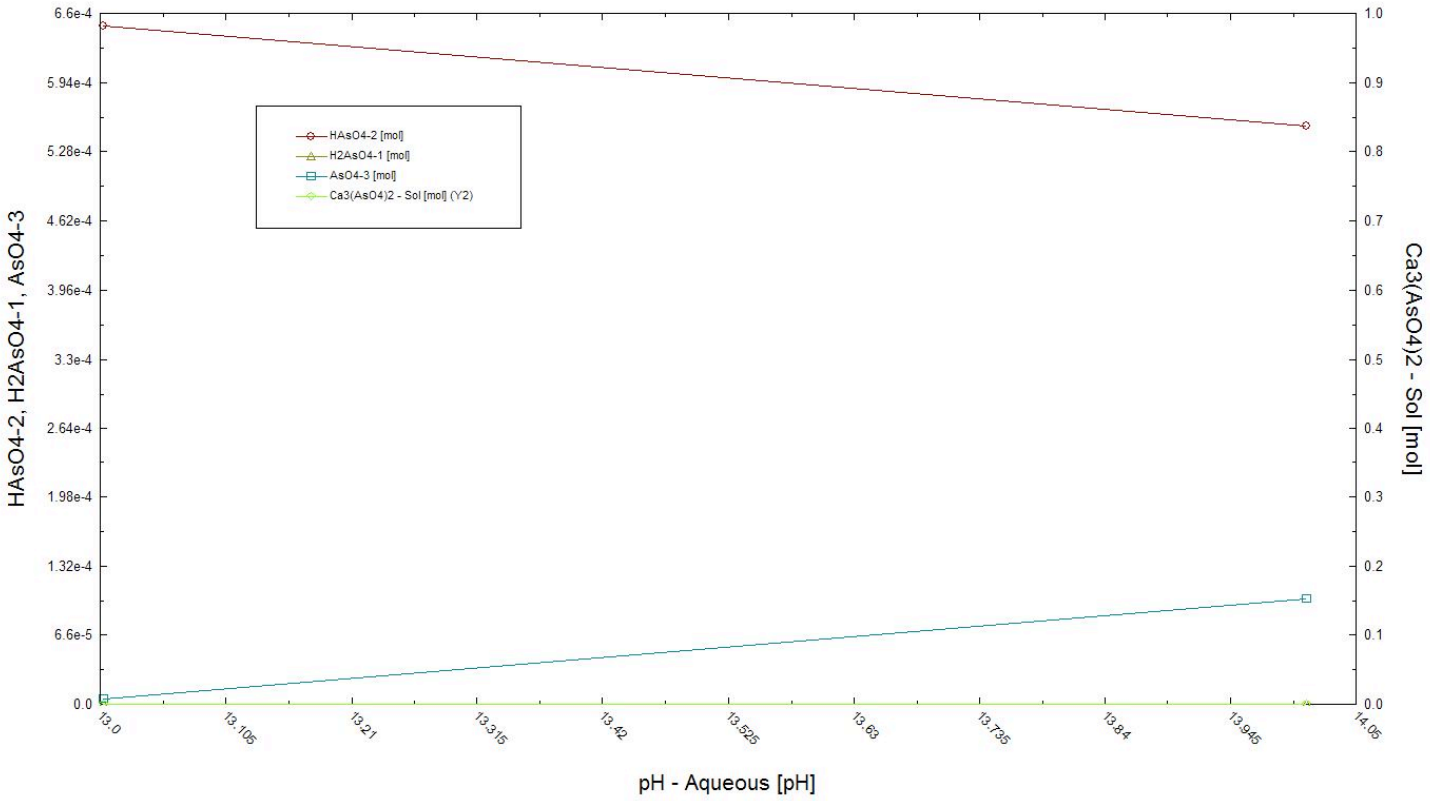


Figure 4-9 Concentrations of dominant As forms with the effect of pH in base titration

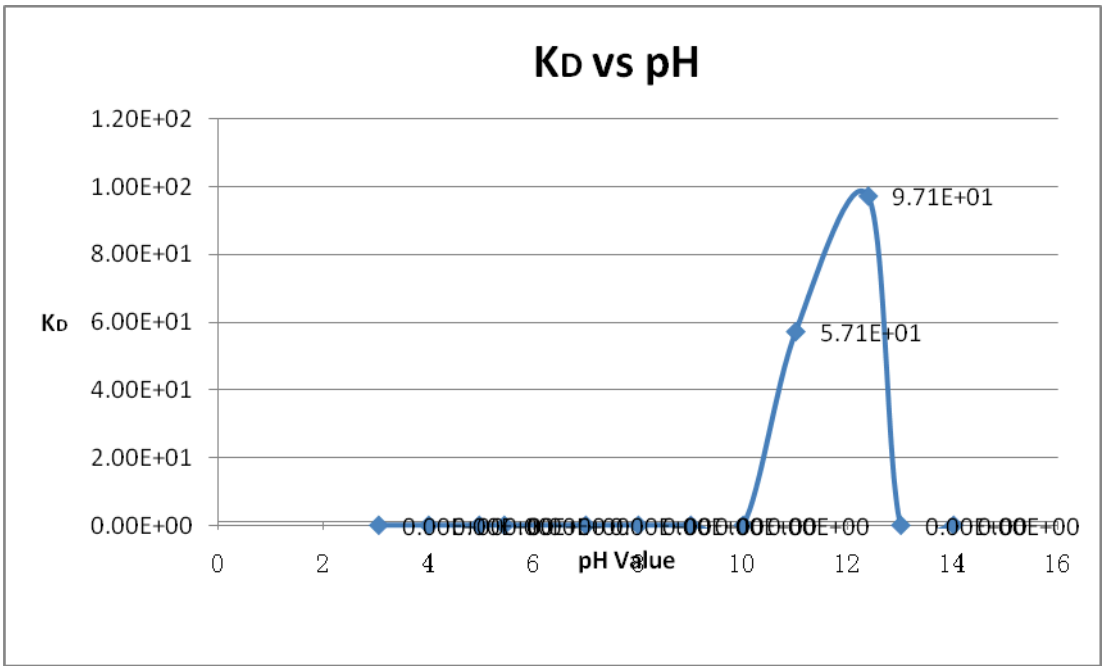


Figure 4-10 Distribution coefficient (K_D) vs pH value

4.3.1 Adsorption of As (V) onto Fly Ash Simulation

This is the study on the adsorption of As (V) as in the form of As_2O_5 on to the typical type F fly ash by Jianmin Wang, Tian Wang, Joel G. Burken, Charles C.Chusuei, Heng Ban, Ken Ladwig, C.P.Huang [47]. The fly ash component weight percent and the inflow parameters are shown in Table 4-9.

The simulation results are listed in Table 4-10. From the results it is very clear that for type F fly ash solution there are no obvious insoluble arsenic compounds that can exist in the solutions. It is also clear shown in Figure 4-11 and Figure 4-12. From the figure it is noted that all the aqueous arsenic compounds concentrations have been changed during the both acid and base titration processes. The dominant arsenic compound in the solution is still $HAsO_4^{2-}$ which is similar to type C fly ash and there are no solid arsenic compound in the solution. As mentioned above, the reason for this effect is due to the low component weight percent of CaO in type F fly ash. The CaO weight percent in this study is 0.83% therefore it is responsible for the absence of solid arsenic compound. However, compared the results with the original experiment results Figure 2-4, the soluble arsenic concentration has the different trend. The arsenic stays constantly soluble throughout the whole titration process in the simulation, from Figure 4-11 and Figure 4-12; the soluble arsenic concentration in Figure 2-4, however, minimum arsenic release was observed between pH range between 3 and 7.

At pH values above 7, the soluble arsenic concentration also increased and reached the maximum at pH around 12. The reason for this discrepancy is due to the following facts: First, the leaching behavior of arsenic process is not only based on the concentrations in both sold and liquid forms, it also involves the surface chemistry, which takes place in non-equilibrium conditions. Take the results in Figure 2-4 for example. The dissolution of ash particles under acidic conditions might contribute to the high soluble arsenic concentration. When pH is between 3 and 7, most of the aqueous arsenic species were readily adsorbed; At pH greater than 7, the decrease of all the protonated surface sites would be the main cause of the arsenic release increase.

Table 4-9 Major components weight percent of fly ash and inflow parameters

Inflow Parameters			Component by Weight Percent (%)									
Fly Ash Mass (g)	Water Mass(g)	As_2O_5 Mass (g)	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	P_2O_5	Na_2O	K_2O	SO_3
10	150	0.01472	0.83	55.7	29.4	4.6	0.79	1.5	0.11	0.32	2.3	0.55

Source: Jianmin Wang, Tian Wang, Joel G. Burken, Charles C.Chusuei, Heng Ban, Ken Ladwig, C.P.Huang, 2008, ”Adsorption of arsenic (V) onto fly ash: A speciation-based approach”, Chemosphere 72 (2008) 381-388.

Table 4-10 Simulation results and concentrations of dominant As forms

Simulation Results								
Single Point Calculation								
Fly Ash pH=7.60972								
Survey Calculation Aq=Aqueous Phase Sol=Solid Phase Unit:(mol)								
pH	$As(OH)_2Cl_3$ (Aq)	$FeAsO_4$ (Aq)	H_3AsO_4 (Aq)	AsO_4^{-3} (Aq)	$Fe(HAsO_4)^{+1}$ (Aq)	$H_2AsO_4^{-1}$ (Aq)	$HAsO_4^{-2}$ (Aq)	$Ca_3(AsO_4)^2$ (Sol)
3.00336	1.06E-22	3.21E-25	3.64E-07	6.69E-16	9.76E-13	3.54E-06	0.000124188	0
4.0764	1.64E-30	1.26E-26	1.47E-08	1.32E-15	1.98E-15	8.98E-07	0.000127176	0
5.05213	1.59E-35	1.41E-28	1.65E-10	1.26E-14	2.37E-18	9.56E-08	0.000127993	0
6.2853	1.77E-42	5.67E-31	6.64E-13	1.87E-13	5.34E-22	6.35E-09	0.000128083	0
7.60972	0	1.97E-33	2.31E-15	2.29E-12	7.90E-26	4.18E-10	0.000128089	0
7.99258	0	3.39E-34	3.97E-16	5.51E-12	5.63E-27	1.73E-10	0.000128089	0
9.00053	0	3.43E-36	4.02E-18	5.16E-11	5.51E-30	1.77E-11	0.000128089	0
9.99368	0	3.60E-38	4.22E-20	4.92E-10	5.85E-33	1.82E-12	0.000128089	0
11.0223	0	3.11E-40	3.65E-22	5.33E-09	4.75E-36	1.69E-13	0.000128084	0
12.0782	0	2.12E-42	2.48E-24	6.94E-08	2.93E-39	1.35E-14	0.00012802	0
12.9718	0	2.02E-44	2.35E-26	9.22E-07	4.09E-42	1.18E-15	0.000127167	0
14.0313	0	3.07E-47	3.33E-29	2.07E-05	8.72E-46	4.19E-17	0.000107435	0

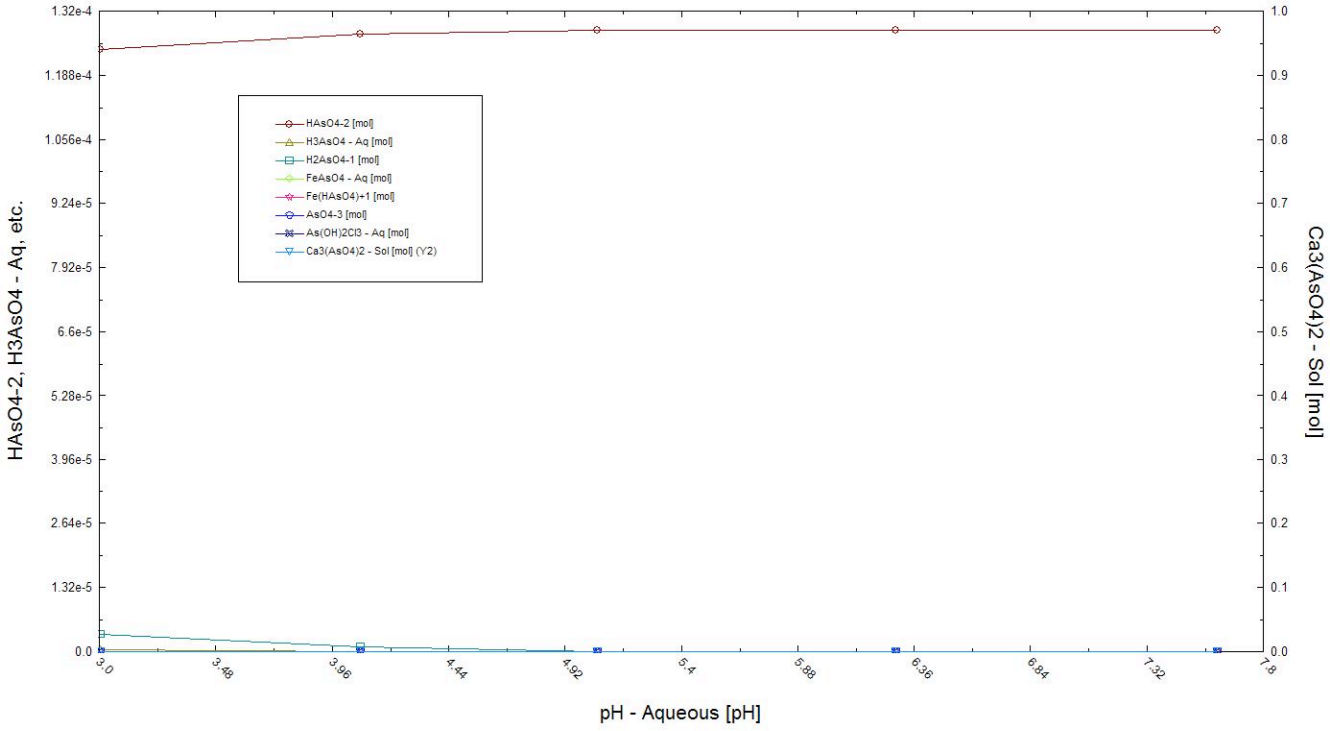


Figure 4-11 Concentrations of dominant As forms with the effect of pH in acid titration

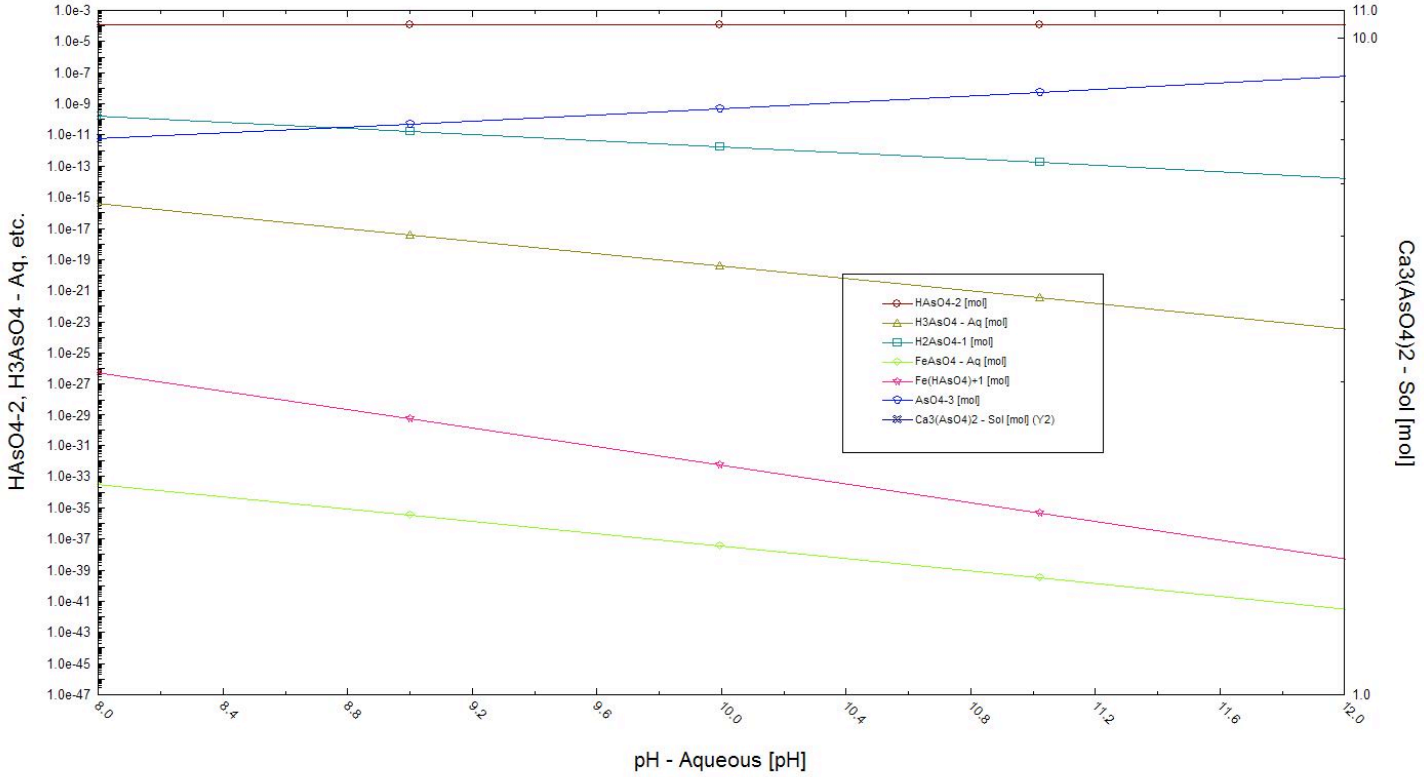


Figure 4-12 Concentrations of dominant As forms with the effect of pH in base titration

Secondly, however, the process above cannot be properly simulated because of the self-limitation of the OLI software. From the previous introduction of the software, it is designed to process all the simulation under equilibrium condition and it cannot consider all the factors that involves with surface chemistry such as surface sites and . Therefore the simulation will have huge discrepancy compared to the actual experiment results.

It is beyond the scope of this thesis to discuss the internal details of the software and import relative coefficient to correct the whole simulation process for type F fly ash. Overall for type F fly ash, the software simulation results would have great discrepancy to actual results. However, from all the simulation results above, it is very clear that for all the type C fly ash, both the single point simulation and composition survey simulation can have reasonably accurate simulation results compared to the actual experiment results and it is noted that for type C fly ash, the maximum distribution coefficient (K_D) is under the equilibrium pH fly ash solution condition.

Chapter 5

Conclusions and Recommendations

Simulation on the pH effect of arsenic separation based on the OLI stream analyzer is proved to be accurate for type C fly ash. In the single point simulation, the percentage errors of simulation results for all the type C fly ash whose equilibrium pH is over 11 is all under 10%. It also can get accurate simulation results for all the type C fly ash whose equilibrium pH between 7 and 9. In composition survey, the simulation of acid/base titration for type C fly ash solution can get the same trend compared to the actual research results based on the type C fly ash. The concentration of arsenic in solid form reaches the maximum at the equilibrium fly ash pH where the concentrations of all aqueous arsenic species reach the minimum and the concentration of arsenic species in aqueous form is shown to give a general trend of decreasing solubility with increasing pH value. From this trend it is easy to get the maximum distribution coefficient (K_D) under the equilibrium pH fly ash solution. For the type F fly ash, the simulation results have great discrepancy and different leaching behavior by the effect of pH values. The reason for this lies in the limitation of software which cannot deal with the surface chemistry that takes place in arsenic adsorption/desorption in storage pond.

From the conclusions above, future research should seek to identify and quantify the impact of other factors such as temperature. The import of relative modified coefficients to improve the simulation results of type F fly ash should also be evaluated. Overall, the OLI stream analyzer can be a useful tool for coal-based power plant industry. It provides an alternative way to analyze the reasonable output species and relative concentrations for type C fly ash in the waste water storage pond under specific pH conditions, which can be of great importance for the power plant to monitor the minimize the environment pollution and meet the future federal regulation.

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List of References

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